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Studies on the Tanning with Glutaraldehyde as an Alternative to Traditional Chrome Tanning System for the Production of Chrome Free Leather.

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Abstract

Chrome tanning is a versatile tanning system, but the pollution problems of chromium due to inadequacy of treatment systems and possible formation of Cr(VI), a carcinogen, have led to search for an eco-friendly and viable alternative tanning system. The present investigation focuses on the development of a novel, high performance and thermally stable aldehyde tannage system to produce chrome free leather by cross linking the NH_2 groups of collagen with glutaraldehyde ($CHO\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CHO$). After as usual soaking, liming, deliming, bating and pickling operations the pickle pelts were tanned with glutaraldehyde and other syntans. This developed chrome free tanning process produce crust leathers exhibiting thermal stability >85^{O}C and reducing the TDS value with 0% emission of Cr-salt in tannery discharge.

Key words : Eco friendly tanning system, Chrome free leather, Crust leathers

Introduction

The tanning industry is one of the oldest and fastest growing industries in South and Southeast Asia but tightening environmental regulations have greatly impacted the operation of tanneries throughout the world. This is because in the leather industry from 1000 kg of raw hides, yield only 150 kg leather and the remaining are 150 kg split, 700 kg solid waste and 30 m^3 of effluent containing 400 kg dissolved and suspended wastes. In this huge amount of tannery waste, chromium salts are considered to be the most heinous element which is used in chrome tanning stage as basic chromium sulphate. So polluting nature of chromium salts has placed chrome tanning under severe criticism owing to ecotoxicological objections, although chrome tanned leathers do possess

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many significant advantages. For these reasons a viable alternative to chrome tanning system is of paramount interest for the production of leathers similar to those of conventional chrome tanned leathers. From the updated scientific literature survey it is found that many attempts have been taken to produce chrome free leather using iron-complexes, synthetic resins with aluminium and titanium, tara-aluminium tanning, wet white pretannage and aldehyde/polymer combination etc. (Balasubramanian and Gayathri, 1997; Gangopadhyay *et al*, 2000; Palop, 2003; Vitolo *et al*, 2003; Palop, 2000). But these processes suffer from various disadvantages such as aluminium tannnage gives inferior shrinkage, and light-fastness, titanium tannage gives full leathers with yellowish tinge, titanium tannins are also expensive. Using vegetable tannins the leather can not achieve the characteristics like chrome tanned leather.

The research reported in this paper seeks to overcome the above disadvantages using glutaraldehyde as a pretanning agent and to minimize the environmental impact of chrome tanning.

Materials and Methods

Raw materials

The brined goat skins and cow hides were obtained from commercial hide brokers. Several experiments were carried out using freshly flayed goat skins of average weight 1kg and average areas 5 sq. ft. and cow hides of average weight 10 kg and average area of 20 sq. ft. obtained from local slaughter houses.

Equipments

In the pretanning step stainless steel drum of 18" width and 36" diameter were used. The speed of the drum was 4 to 20 rpm. For subsequent operations upto crust and finish as usual machinaries were used.

Chemicals

The following chemicals were employed in the pretanning step of leather processing glutaraldehyde, sodium meta bi-sulphite, syntan, sodium bi-carbonate and fungicide.

All the chemicals were commercial grade products. The chemicals employed in subsequent operations were those normally used in leather industry.

Optimization of glutaraldehyde for pretanning

The percentage glutaraldehyde offer was varied from 0.5% to 3% for tanning along with the fixed amount of the syntan and other chemicals. Pickled pelts were used for tanning experiments. The shrinkage temperature of various tanned leathers were determined and benchmarked for selecting the optimum amount of glutaraldehyde.

Tanning processes

For both glutaraldehyde tanning and chrome tanning operations of leather processing the raw hides were converted into pickled pelt by traditional beam house operations. Then the pickle pelts were converted into wet white and wet blue leather and subsequently to crust leather by the following processes.

Table-I. Processing steps

Glutaraldehyde tanning for the production of crust leather	Chrome tanning for the production of crust leather
Tanning by 2.5% glutaraldehyde, 1 % sodium meta bi- sulphite, 50% water, 2% naphthalene based syntan, 0.6% sodium bi-carbonate and 0.2% fungicide.	Tanning by 6% basic chromium sulphate and 2% chrome syntan.
Then samming, splitting and shaving operations were done for the production of wet white leather.	Then samming, splitting and shaving operations were done for the production of wet blue leather.
Neutralization by 1.5% Neutralizing syntan. Retanning by 4% acrylic syntan, 6% vegetable tannin and 4% resin syntan.	Neutralization by 1.5% Neutralizing syntan. Retanning by 4% acrylic syntan, 6% vegetable tannin and 4% resin syntan
Then fatliquoring and dyeing were done for the production of crust leather.	Then fatliquoring and dyeing were done for the production of crust leather.

Determination of shrinkage temperature

Samples of tanned leather were tested in the wet state, just after tanning. This means that immediately after tanning the specimens were washed in running water and squeezed several times with a blade to eliminate the excess water and tanning solutions. Triplicate leather samples for a total samples dimension of 50 x 3 mm for a thickness less than 0.3 mm were used for shrinkage temperature determination. The method used for shrinkage temperature determination is codified in the international norm (International leather union) for leather. The heating rate used was of 1.50 C/min.

Tanning discharge analysis

The waste water discharge from tanning operation was analyzed for some common characteristics of waste water which are important in assessing the potential for water pollution like pH, BOD, COD, total solids, dissolved solids, suspended solids, chloride, total chromium etc. according to the standard method (Clesceri *et al*, 1999).

Sampling for physical and chemical analysis

In each experiment the hides and skins were sampled after each processing stage (Standard practice for sampling, 2002. For physical testing square (10" x 10") samples were taken 4" away from the foot of the tail and 2" away from the back bone. For chemical analysis rectangular pieces of leather measuring 6.5" x 2.5" were taken from each side representing the butt, belly and shoulder portions.

Physical analysis

The main physical properties namely thickness of the leather, tensile strength, extension, ball brust of controlled leather and those of tanned with glutaraldehyde, conditioned at 80 $\pm$ 4^{O} F and 65 $\pm$ 2 % R. H. for 48 hours are assessed in accordance with standard methods (Dutta, 1999) Each value reported is an average value of four samples.

Chemical analysis

Volatile matters, ash, hide substance, chrome content of both the leathers tanned with glutaraldehyde and chrome were determined by the official methods of analysis of SLTC (Society of Leather Technologist and Chemists, 1996).

Results and Discussion

Effect of glutaraldehyde on the shrinkage temperature and visual characteristics of leather To optimize the amount of glutaraldehyde for tanning different amounts of glutaraldehyde were used and the results of shrinkage temperature and visual assessment data of leather are shown in Table II.

From the table it is evident that with increase in the amount of glutaraldehyde added considerable increase in shrinkage temperature of leather was obtained using glutaraldehyde upto 2%, with further increase in glutaraldehyde to 2.5% there is only slightly increase in shrinkage temperature of tanned leather.

Table-II. Shrinkage temperature and visual characteristics of leather at different percentages of glutaraldehyde

Glutaraldehyde added (%)	Shrinkage temperature (Ts^{O}C)	Visual assessment scale (0-10)*	
		Grain characteristics	Fullness
0.5	80	8	5
1.0	80	7	6
1.5	82	7	7
2.0	84	7	8
2.5	85	7	9
3.0	85	6	9

* The scale of 0-10 indicate 0 for poor and 10 for very good.

Further increase in glutaraldehyde offer results no change of shrinkage temperature.

The increase in the offer of glutaraldehyde to 3% results in the leather of coarse gain. Empty leathers have been obtained when 0.5% glutaraldehyde was used and the fullness of the leather increases with the increase of glutaraldehyde added upto 2.5%. Considering both the shrinkage temperature and the properties of the tanned leather, 2.5%

glutaraldehyde (based on the pelt weight) has been found to be the optimum offer.

Tanning discharge analysis

The discharge from chrome tanning and glutaraldehyde tanning were analyzed for the parameters which are listed in Table III.

From the table it is found that though the BOD and COD in the discharge of glu taraldehyde tanning is high but the total solids and chloride are much less in glutaraldehyde tanning discharge. From the table it is revealed that there is no discharge of chromium in the effluent of glutaraldehyde tanning. So in environmental aspects the glu taraldehyde tanning is much more acceptable than the conventional chrome tanning.

Table-III. Characteristics of tanning discharge.

Parameter	Chrome tanning	Glutaraldehyde tanning
pH	2.5 - 4.0	3.0 - 4.0
BOD 5 day at 20^{O}C (Total)	350 - 800	500 - 1000
COD (Total)	1000 - 2500	1200 - 3000
Total solids (TS)	30,000 - 60,000	20,000 - 40,000
Dissolved solids (DS)	29,000 - 57,500	25,000 - 48,500
Suspended solids (SS)	1000 - 2500	800 - 1800
Chloride (as Cl)	15000 - 25000	13,500 - 22,000
Total chromium (as Cr)	1500 - 4000	0

All the values except pH are expressed in mg/L.

Physical parameters

The physical parameters of both glutaraldehyde tanned and chrome tanned leathers are listed in Table IV. From the table it is found that the physical properties of the glutaraldehyde tanned leather is comparable or in some cases better than the leather tanned by conventional chrome.

Chemical properties

The chemical properties of the leather tanned by glutaraldehyde and chrome are shown in Table V. From the table it is found that in wet white leather percentage of Cr_2O_3

Table : IV. Physical properties of the tanned leather

Physical properties	Glutaraldehyde tanned leather	Chrome tanned leather
Thickness (inches)	0.065	0.064
Tensile strength (psi)	2256.3	2255.80
Extension (%)	44.10	45.21
Ball brust (lbs)	124.50	25.10

Table :V. Chemical properties of the glutaraldehyde tanned leather and chrome tanned leather after shaving

Assessment	Chemical composition of pretanned leather after shaving (wet white)	Chemical composition of chrome-tanned leather after shaving (wet blue)
Volatile matters	9.8%	3.0%
Sulphated total/ash	1.3%	2.3%
Hide substance	29.5%	75.2%
Cr_2O_3	---	4.8%

is nill because no chrome is used in wet white leather. In wet white leather ash and hide substance is less than chrome tanned leather but percentage of volatile matter is higher in wet white leather.

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