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Effects of Chrome-Syntan-Vegetable Combination Retannage and Polymerization *(in situ)* on the Internal Membrane of Bovine Stomachs for Exotic Leather

Muhammad Saeed Khan* and S R H Jafri

Leather Research Centre, PCSIR, D/102, South Avenue, SITE, Karachi, Pakistan

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Internal membrane of bovine stomach with poor hide substance (the leather making material), a solid waste from slaughter house, was processed into exotic leather for value-added goods like ladies hand bags, purses, wallets etc. Pure vegetable, synthetic/vegetable tanning or tanning of an unlimed membrane gave unsatisfactory leather. Its thickness, hide substance, leatherity, thermal stability and strength properties were considerably increased through polymerization *in situ* (urea formaldehyde) followed by chrome tannage and synthetic retanning, and chrome-syntan-heavy vegetable combination retannage. Resin finishing contributed additional strength and beauty to the leather. In the former case the average thickness and shrinkage temp. (Ts) were 0.8 mm and 135°C respectively with diminished surface area and coarse shrunken grain affect. In the later case the average thickness and Ts were 0.7 mm and 128°C respectively with improved stability, cutting value, better area yield with prominent natural grain patterns and about 9% more weight gain than the former case. The tensile strength in both the cases was low i.e. 34.8 kg/cm^2 but was within the limits of fancy light leathers.

Key words: Exotic leather, Heavy vegetable retanning, Polymerization.

Introduction

Leather, especially the exotic leather for fancy articles regardless of its origin, is an international commodity of commerce.

During a visit to slaughter house at Karachi it was noticed that the internal membrane of bovine stomach which appeared to be a thin skin was of not much use. It was either treated as solid waste or used in poultry feed.

Investigations were made to convert the membrane into fancy leather (Fig 1) suitable for value-added goods like ladies hand bags, purses, wallets and other items. The leather had a distinct and an attractive grain, high thermal stability (135°C), improved hide substance and fullness. The strength properties attained by the leather such as tensile strength, resistance to repeated flexing etc., were within the limits of exotic leather (maintaining the cost of production).

The processes worked out for making the fancy leather from the non-conventional source will provide an alternative source of leather and will generate an extra income for leather producers. Articles made of this leather (Fig 2) are excellent in appearance, durable and retained their shapes.

*Author for correspondence

Materials and Methods

The innermost membranes of bovine stomachs are falyed by hands in slaughter house. The area of stomach layers approximate that of a goat skin, possess epidermal layers and dermis (Barat *et al* 1972). There are few subcutaneous tissues on flesh side, three heterogeneous patterns visible on grain and three to four plain strips. Another area of the grain is densely covered with finger like projections called villi whereas the remaining portion of the grain is almost plain. The region of the grain containing villi and the plain strips make the leather exotic. It is observed that the strips are thinner than the rest of the membrane. They are also supple and free from villi. The villi have harsh feel like an emery paper in contrast to normal region of the membranes. The villi resemble the towel like fibres with interstitial distance of approximately 0.1 mm. The ox membranes are relatively thicker and have large surface area as compared with female buffalo membranes. When de-skinned, the ox memberane is yellowish white and that of the buffalo is white.

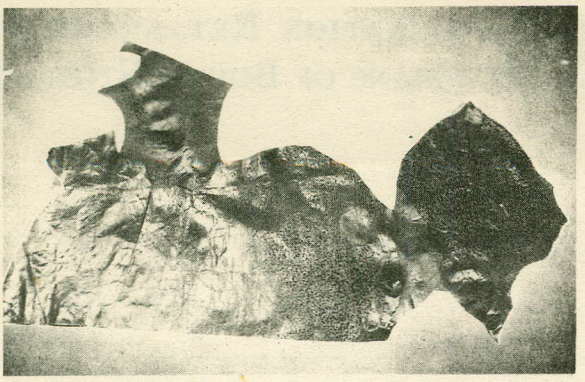

Fig 1. Fancy leather from the internal membranes of bovine stomachs.

Fig 2. Ladies hand bags fabricated from the internal membranes of bovine stomachs leather.

It is also observed that some membranes particularly those of old animals have insects on their grain, *viz.* nematodes, cestodes and trematodes. The membranes have characteristic smell which diminishes gradually in the course of leather processing and the final dried processed leather is free from the peculiar smell. A typical analysis of the membrane is given in Table 1.

The fresh membranes of bovine and female buffalo were collected from slaughter house, well washed, hanged to air dry and analyzed for inorganic matters and extractable substances from *n*-hexane (non-polar) and dichloro methane (polar). Shrinkage temperatures were also determined. After processing, the leathers were finished. Samples for tensile strength and % elongation at break were tested in direction perpendicular to each other as per ASTM D412 having a uniform speed of separation of jaws of 100 ±2 0 mm per minute.

Resistance to repeated flexing was determined according to IUP/20. Ts of retanned leather were noted in liquid paraffin. For rub fastness SATRA apparatus was used.

To convert the membranes into leather, four different techniques *viz.* chrome tanning of unlimed pelts, synthetic/vegetable tanning, polymerization *in situ* and chrome-syntan heavy vegetable combination tannages were adopted. The processes are given below in some detail.

1.Chrome Tanning of Unlimed Pelts. Properly soaked membranes were picked in a drum (12 rpm) and 6% Chrome PAK (basic chromium sulphate, 24% Cr_2O_3) was added on drained soaked weight. Tanning was ended at pH 3.8 in 5 h. After four days aging, the leather was neutralized to a cut edge pH 5.5 in a buffer system. Retannage was carried out in a drum (16 rmp). As retanning agent, 5% Tanigan QF (replacement syntan) was added. The leather was dyed and 10% mixture of sulphonated, sulphited and synthetic fatliquor emulsified in 10% water (60°C) was added. It was drummed for 1 h and horsed up overnight. Next day it was wet toggled and allowed to dry at room temperature.

2. Tannages/retannages of de-limed and Bated Membranes. The soaked weight of bovine membranes having nearly equal surface area and thickness was determined. Liming was carried out in a drum (3 rpm) employing 3% sodium sulphide, 8% hydrated lime and 200% water (20°C) for 48 h. Drummed 10 min at the start and then 2 min every 3 h. Then the pelts were put in a 6% milk of lime for 48 h. The pelts were delimed, bated with 1% Oropon OR (pancreatic enzymes), lightly degreased and treated as follows. Two membranes were used for each treatment.

2.1 Synthetic/vegetable Tanning. Membranes were lightly pickled to pH 5.5. To this added 6% Tanigan OS (replacement syntan), drummed 30 min followed by 16% blend of sulphited mimosa and quebracho in three feeds; (40 min each). Further drummed for 1 h then left overnight in the same bath. Next day fatliquored with 12% mixture of sulphonated, sulphited and synthetic fatliquor emulsified in 10 % water (45°C), horsed up overnight, wet toggled the next day and allowed to dry at room temperature.

2.2 Polymerization in Situ. To the de-limed and bated membranes, 7% urea on pelt weight was offered and drumming continued for 1 h. Then the required quantity of formaline (actually 10% on pelt weight) was added for the formation of dimethylol urea by condensation (Muchy and Castellu 1953). The methylol (di) compounds were thought to polymerise *in situ* through interaction between the hydroxyl and amino groups with the elimination of water (Priest 1950).

NH_2	$NH\text{-}CH_2OH$	$NHCH_2OH$
|	|	|
$C = OHCHO$	$C = O \rightarrow$	$C = O$
|	|	|
NH_2	NH_2	$NHCH_2OH$
Urea	Monomethylol Urea	Dimethylol Urea

Treating the delimed and bated membranes with replacement syntan followed by condensable vegetable tanning and fatliquoring yields a product with papery feel, dried out hard and brittle and high degree of firmness with very low strength. By varying the pre-tanning conditions, offer of material and drumming time, it has been found that vegetable tanning can be carried out successfully on all known types of raw stocks from sheep splits to that of the hide of a steer (Anon 1990). Experiments performed reveal that a suitably modified membrane for vegetable or vegetable/synthetic tanning does not give satisfactory leather. It is particular to the fibre structure of the membrane.

Both the villi and plain strips on grain persist in the final leather. The villi are softened, swollen and their harshness is minimized to a greater extent by the action of sharpeners and lime. The harshness is also affected by the type of tannage, retannage and fatliquors employed in the course of leather processing. They are harsher after vegetable tannage as compared with mineral tannage.

Chrome tannage is the predominant tannage for tanning the memberane because tanning imparts its leathery feel and fullness.

Inferior skins with poor hide substance, on treatment either with the polymerization tannage followed by chrome retannage, or with heavy combination retannage yield quality leather fit for case, wallet and glove leather, pertaining to high Ts, improved hide substance and thickness (Hasan *et al* 1984). Total nitrogen content in leather is an important factor which determines hide substance in leather. Empty leathers are partially lacking in hide substance. As shown in Table 2 that as a result of polymerization tannage and heavy vegetable retannage, the nitrogen contents of leather have reached 36.5% and 28.7% respectively which indicate that the leathers are fuller and not empty.

Thickness of such leathers is not uniform throughout the surface. It is difficult to shave them at uniform gauge as villi on grain interfere during shaving. In fact for making articles from this type of exotic light leather, no shaving is required. Normal requirements of fancy leather for ladies hand bags, wallets, purses etc. are in the order of 0.6 to 0.8 mm. Fancy articles may be fabricated from the leather of bovine membranes having thickness in the range of 0.7 and 0.8mm.

Leathers processed of surface areas 0.92 m^2 and 1.0 m^2 weigh only 0.32 kg and 0.35 kg respectively which implies that they are light weight but possess large surface area.

Any treatment or tannage on collagenous matter does not enhance the tensile strength (O' Flaherty 1956). Low values of tensile strength reported in Table 2 are due to the nature of original fibre structure of the membranes.

Presence of free acids is the main cause of damaging the leather fibres. Low pH difference value of the leathers show that they contain no free acids.

Thermal stability is an important property of leather. High values of Ts attained in experiment 2.2 (Ts 135°C) and in experiment 2.3 (Ts 120°C) render the leather resistant to wetness and dry heat.

Polymerized (urea formaldehyde) synthetic retanned membranes have coarse shrunken grain thus diminishing the natural grain look. On the other hand chrome-syntan-heavy vegetable retanned membranes have good form stability and cutting value by filling the voids with vegetans alongwith prominent natural grain patterns. The softness in both the cases will depend upon the type and quantity of fatliquors employed. The leathers may be dyed with anionic dyes but it was observed that villi always attain darker colour than the actual grain.

The memberanes may withstand the pounding action of drum. However, the mechanical action on the tender membrane in all the stages before coming in contact with the mineral tannins should be kept as minimum as possible in order to avoid undue damages.

Drying the Membranes After Retanning. Drying methods involved mechanically holding the leather in an extended position. It yielded larger surface area and prevented attractive forces within the fibers from making it uneven (Thorstensen 1985). After retanning, colouring and fatliquoring, the leathers were wet toggled with relatively low tension to remove wrinkles and creases, providing a flat surface for finishing. It was observed that hang dried leather in air without tension produces relatively softer and thicker leather but badly wrinkled leather as a result of such drying finds no use for making leather articles.

Finishing. The leathers were semi-aniline finished employing casein free pigment, acrylic based resins, aniline dyes, auxiliaries and nitrocellulose lacquer as top coat. In finishing, care was taken not to spray too heavy coats on villi in order to prevent them sticking together.

No appreciable damages to the finishes or to the finished leather were observed as a result of repeated flexing.

The exotic finished leather from the internal membranes of bovine stomachs have sufficient dry (rating 3-4) and wet rub resistance (rating 3) and is fit for making small fancy leather goods.

Table 1

Physico-chemical studies of internal membranes/villi of bovine & female buffalo stomachs

S. No.	Shrinkage temp. raw membrane Ts (°C)	Shrinkage temp. Villi Ts (°C)	Ash raw membrane (%)	Ash villi (%)	Extractable substance raw membrane with *n*-Hexane (%)	Extractable substance villi with *n*-hexane (%)	Extractable substance raw membrane with dichloro-methane (%)	Extractable substance villi with dichloro methane (%)
Ox	68-70	---	9.8	6.8	1.9	9.1	0.3	0.9
Female buffalo	68.70	---	8.2	5.7	1.6	2.8	0.3	0.5

NB. Ash and extractable substances were determined on moisture free basis.

Table 2

Physico-chemical studies acquired by the polymerized and chrome-syntan-vegetable combination retanned membrane

Art of tannage and/or retannage offered	Total Nitrogen in leather (%)	Max. thickness achieved by leather (mm)	Surface area of leather (m^2)	Wt. of leather processed (kgs)	Resistance to repeated flexing (20,000 flexes)	SATRA dry rub fastness (1000 cycles)	SATRA wet rub fastness (200 cycles)	Tensile Strength (kg/cm^2)		Elongation at break (%)		pH of leather	pH difference value	Ts °C
								lateral	longi-tudinal	lateral	longi-tudinal			
	1.	2.	3.	4.	5.	6.	7.	8.		9.		10.	11.	12.
Polymerization *in situ* chrome tanning/synthetic retannage	36.5	0.8	0.92	0.32	Feeble damage of finish	Grade 3-4	Grade 3	34.8	19.3	35.9	37.8	4.4	0.7	135
Chrome-syntan heavy vegetable combination retannage	28.7	0.7	1.0	0.35	Feeble Damage of finish	Grade 3-4	Grade 3	30.7	14.3	13.8	16.5	4.1	0.6	128

NB. For physical tests, 5 to 9 finished membranes were used.

To this bath 6% Chrome PAK was added and main tanning was ended at pH 4.0 in 6 h.

After aging the wet blue membranes were neutralized to a cut edge pH 5.5, retanned with 5% Tanigan QF, dyed and fatliquored employing 10% mixture of sulphonated, sulphited and synthetic oil. Horsed up overnight, wet toggled and allowed to dry at room temperature. The leather was semi-aniline finished from grain side.

2.3 Chrome-syntan-heavy Vegetable Combination Re-tannage. To the de-limed, bated and pickled membranes, 6% Chrome PAK was added and tanning was ended at pH 3.8 in 6 h.

After aging the leather was neutralized to a cut edge pH 5.5, then 3% Tanigan OS (replacement syntan) was added, followed by 14% sulphited mimosa in two feeds, (40 min each). The leather was fatliquored with 10% mixture of anionic oils, horsed up overnight, wet toggled dried at room temperature and finished as before.

Results and Discussion

According to Gustavson (1956) liming activates certain protein groups, plumping the hide by water uptake, 'opening up of fibre bundles' bringing about lateral splitting of the individual fibres, saponifying fats and modifying or removing the additional proteins such as those present in the interfibrillary matter, reticulin and the pelt into a suitable state for tanning. Hence, an unlimed membrane is tanned unevenly into a bony hard mass with lack of fullness having poor strength properties. The villi of such a leather very harsh like an emery paper. The leather so obtained is substandard and practically useless. Thus an unlimed membrane gives an ugly leather even retanning with syntan does not improve its character.

Conclusion

The process of utilization of internal membrane bovine stomachs into exotic leather will reduce the solid waste pollution load and will also provide an alternative source of leather for value-added items.

The cost of the basic raw material is several times less as compared with a goat or sheep skin. The machinery involved for the processing is simple and traditional. Labour time and cost of processing is further minimized as fleshing, scudding, splitting, shaving, buffing, plating and milling operations are not involved in manufacturing the leather.

Tanning with basic chromium sulphate of polymerized membrane (urea formaldehyde) followed by synthetic retannage, and chrome-syntan heavy vegetable combination retannage are the two methods which may be successfully employed to convert the membranes into exotic leather.

The processes of making the exotic leather from the non-conventional source were carried out on small scale and may be adjusted to pilot scale. It is expected that the export of leather articles prepared from the membrane would enhance foreign exchange earning of the country.

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