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Alternative methods for Salt free / Less salt short term preservation of hides and skins in leather making for sustainable development – A review

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ABSTRACT

During the leather processing, large quantities of the salt as sodium chloride, about 30-50 % (% w/w on raw weight) is applied for short term preservation of hides and skins, which subsequently leaches out from the skins/hides and end up in waste streams. This raises a serious environmental concern as well as total dissolved solids (TDS) problem in the wastewater, for which there is no viable treatment method available. Remediation measures such as Reverse Osmosis (RO) or Ultra Filtration (UF) could only separate salt from these waste streams and end up as salt sludge, which necessitates Secured Land Fill (SLF) for disposal option. There are some concerns for SLF as it requires Land area as well as possible leaching due to highly soluble nature of Sodium chloride. Therefore, there is a pressing need for developing an alternative methods for Salt free / Less salt short term preservation of hides and skins. In this regard, Research and Development work is being carried out worldwide and several reports are available. Therefore, it would be beneficial to review and analyze the salt free alternative preservation methods. Even though, some reviews on this topic has been reported earlier, they have not taken into account the patent literature available on this subject. The present paper reviews various alternative methods for Salt free / Less salt short term preservation of hides and skins, taking into account both patent and other publications on this subject.

KEY WORDS

Alternative methods, salt free, less salt, short term preservation, hides, skins, leather processing, total dissolved solids (TDS), environment, salt pollution, eco-benign

INTRODUCTION

The objective of leather processing is to convert putrescible raw skin/hide into useful material called leather by the process called 'tanning'. There is a need for short term preservation of raw hide/ skins called as *curing,* essentially required during transport or temporary storage of raw stock prior to tanning process. The objective of curing is to preserve the raw skin/hide temporarily against the microbial attack. The application of common salt in curing process works on the principle of dehydration. Generally, the principle of dehydration of skin/hide is employed to bring the water content from 60% to 25% to control the bacterial action, as their activities are known to be retarded in lower moisture content. Conventionally, about 30-50

% (% w/w on raw weight) of sodium chloride is applied on the flesh side of the skin/hide as a curing method which can bring down the moisture content to the required level by osmotic process [1].
During the leather processing, large quantities of the salt that has been used for short term preservation are leached out from the skins/hides. This raises serious environmental concerns as well as total dissolved solids (TDS) problem in the wastewater, for which there is no viable treatment method available. Remediation measures such as Reverse Osmosis (RO) or Ultra Filtration (UF) could only separate salt from these waste streams and end up as salt sludge, which necessitates Secured Land Fill (SLF) for disposal option. There are some concerns for SLF as it requires land area as well as possible leaching due to highly soluble nature of Sodium chloride. Eco-benign alternatives attempted so far, for salt-free based preservation methods have not provided successful commercial viability. Even though some reviews on this topic have been reported [2], they have not taken in to account of patent literature available on this subject. The present paper reviews various alternative methods for Salt free / Less salt short term preservation of hides and skins, taking into account both patent and other publications. The limitations and drawbacks associated with each alternative method have been analyzed.

Approaches towards the development of alternative salt free preservation

There are several approaches towards development of alternative salt free preservation listed below:

a. Alternative non-toxic chemicals to salt
b. Use of Eco-benign materials
c. Use of Natural materials
d. Application of Electromagnetic waves
e. Use of Drying methods

Hence, available literature on alternative salt free preservation methods mostly fall in any one of the above listed methods.

Mechanism of short-term preservation of hides and skins

Mechanism for short-term preservation of hides and skins shall be broadly classified as follows,

a. *Bacteriostatic action:* due to dehydration of water present in hides and skins from 60% to 25%.
b. *Antimicrobial Effect:* due to Interaction of preservative agents with Bacteria or Enzymes present in hides and skins.

Patent Literature on the Salt free and Less salt short term preservation

Brosse et al. [3] have provided the use of superabsorbent polymers for treating raw skins, corresponding compositions, methods and resulting treated skins. The drawbacks are the product of polymer and non-biodegradable, which pose environmental problems.
Rother et al. [4] have studied the use of combinations of active compounds composed of phenolic or heterocyclic active compounds and azole compounds for the preservation of animal hides and leather. The drawbacks are toxic product, which may also pose environmental problem.
Bonjour et al. [5] filed a patent, wherein a fungicidal composition the form of an aqueous emulsion is formed from 3-iodo-2-propynyl-N-butylcarbamate (IPBC), 2-(thiocyanomethylthio) benzothiazole (TCMTB), polyoxyethylene triglyceride, polyalkylene glycol ether, xanthan gum and dipropylene glycol. The drawbacks are the invention related to the product, which has fungicides and may not be suitable for action against bacteria for preservation of skins/hides.

Rother et al. [6] patent discusses the composition of a mixture of a phenolic compound and an azole or morpholine compound to protect animal hides and leather against microbes. The drawbacks are the toxic product, which may pose environmental problem.

Bonjour et al. [7] a patent, whit stable aqueous fungicidal emulsion of 2-(thiocyanomethylthio) benzothiazole (TCMTB) and 3-iodo-2-propynyl-n-butylcarbamate (IPBC). The drawbacks are the invention related to the fungicide product, which is not suitable for action against bacteria for preservation of skins/hides.

Rother, et al. [8], produced the method of using a mixture of a phenolic compound and an azole or morpholine compound to protect animal hides and leather against microbes. The drawbacks are the invention related to the toxic patent, which poses environmental problem. Relates only to the method of application of patented.

Rother et al. [9] a patent, studied a preservation process that is environmentally safe and that prevents bacterial or enzymatic decomposition of the hides, the hides are treated with CO_2 immediately after being pulled off. The drawbacks are - the invention related to the process involves operation difficulties such as sotrag, delivery and handling gas. CO_2 application also affects eco-system.

Munch et al. [10] patent, wherein the process for the short-term preservation of rawhides and skins with an alkali metal chlorite solution additionally contains compound with hydrogen or C-alkyl, hydrogen or an alkali metal atom. Because of their hydrotropic action, the addition of these compounds improves uniform penetration of the preservation solution into the hide. The drawbacks are the product containing alkali metal chlorite that could pose environmental problems.

The patent by Procedes Escaiech Soc D Expl [11], wherein processes for the dressing, partial discolouring and preservation of the natural qualities of skins, leathers, hairs and furs by treatment in an acid aqueous solution of metal salts (other than alkali and alkaline earth salts) and an alkali nitrite, aromatic phenols and amines being also present in the bath. Hydrogen peroxide or like oxidizing agent may be employed for supplementary treatment. The drawbacks are the invention related to the product utilization of toxic chemicals and liberating ammonia, which could pose environmental problems.

The patent by Guenzburg Ury De [12], produces an improved method of preserving and tawing Skins; Tawing hides and skins, raw or tawed, and treating furs. It relates to a process of preservation or tawing of skins with or without the hair, wool, or feathers. The method serves also for bleaching the skins, wool, etc. Also to render them very suitable for dyeing. The soaked and fleshed skins, if to be depilated, are treated with nascent sulphohydrate of calcium sulphide. The hair and adhering flesh then being removed by hand or mechanically. The skins may then be tawed, and immersed in a solution of bisulphite of alumina, to which a small quantity of hydrochloric acid may be added to facilitate the liberation of hyposulphurous and sulphurous acids. The skins are drained and immersed in an ammoniac bath, which produces a white gelatinous precipitate. Neutral chromate of soda may be added to this bath. The skins are now dressed in fulling-mills with a firm paste consisting of wheaten flour, glycerine, and the residues of precipitation of the ammonia bath. The skins may subsequently be dyed and finished as desired. The drawbacks are the invention related to the process utilizing toxic chemicals such as calcium sulphide, which pose environmental problems.

Sant Prasad Gautam [13] a device patent, wherein an apparatus and method of preservation of animal skins/hides which provides an apparatus for curing of raw animal skins and hides for preservation for transportation to tannery industries comprising a lyophilizer having a drying chamber, suction pipe or pipes disposed within said chamber and connected to condenser for trapping water vapours formed in the drying chamber and a vacuum pump a frame disposed within said chamber and having means for hanging the skins and hides. The drawbacks are the patent relates to apparatus not the process/product, which involves operation difficulties.

Sivakumar et al., have filed a patent on the synergistic composition of natural products with less salt 10% for short-term preservation of hide/skins [14]. This could minimize the use of salt to great extent.

Literature on the Salt free and Less salt short term preservation

Bailey et al. studied the preservation of cattle hides with Potassium [15]. However, the drawback is associated with its cost factor and contribution to TDS problem.

The publication by Kannan et al., [16] wherein salt free preservation of skins has been carried out using Poly ethylene glycol employed as the active agent. The drawbacks are the report related to the non-natural product, which could pose environmental problems.

The publication by Kanth et al., [17] wherein salt free preservation of skins has been carried out using *Sesuvium portulacastrum* (*S. portulacastrum*) and halophyte employment as the active agent. The drawbacks are the report related to the product itself containing salt. Since the plant material is grown only on coastal areas, the removal could lead to disturbance of eco-balance in coastal areas.

The publication by Didato et al., [18] wherein salt free preservation of skins has been carried out using Collagenase inhibitors incorporated as preservatives and employed as the active agent. The drawbacks are the report related to the product that is a chemical not based on natural product also potentially expensive.

The publication by Stockman et al., [19] wherein salt free preservation of skins has been carried out using antibiotics such as Doxycycline HCl and employed as the active agent. The drawbacks are the report related to the product that could pose environmental problems, health hazards and could be expensive.

The publication by Bailey et al., [20] wherein electron beam irradiation for preservation of cattle hides in a commercial-scale demonstration was reported. The drawbacks are the report related to the process involving the operation difficulties and health hazards due to radiation effects.

The publication by Kanagaraj et al., [2] wherein less salt preservation of skins has been carried out using a combination of silica gel - environmental friendlier and easy-to-treat powerful dehydrating agent and 5% salt with or without 0.1% of p-chloro meta cresol (PCMC). The drawbacks are the report related to the chemical and not a natural product. Also not eco-friendly due to chlorinated product. The publication by Kanagaraj et al., [21] also discussed the approach to less-salt preservation of raw skin/hide using Silica gel.

The publication by Baily [22] wherein salt free preservation of skins has been carried out using gamma irradiation. The drawbacks are the report related to the process involving the operation difficulties and health hazards due to radiation effects.

The publication by Buechler et al., [23] wherein salt free preservation of skins has been carried out using solvent. The drawbacks are the report related to the process posing health hazards due to organic solvents.

The publication by Hopkins [24] wherein the salt free preservation of skins has been carried out using SO_2. The drawbacks are the report related to the process posing health hazards due to SO_2 gas.

The publication by Hopkins [25] and Bailey & Hopkins [26] wherein preservation of skins has been carried out using Acid-Sulfite. The drawbacks are the report related to the not eco-friendly process, which contributes to TDS.

The publication by Money [27] wherein report on preservation of skins with Use of Zinc Chloride or Calcium Hypochlorite as alternatives to Sodium Chlorite was made. The drawbacks are the report related to the not eco-friendly process, which contributes to TDS.

The publication by Valeika et al., [28] wherein report on preservation using 1% Sodium hexafluorosilicate and 5% Sodium Chloride was made. The drawbacks are the report related to the not eco-friendly process, which contributes to TDS.

Sivakumar et al., [29] have studied the se of Ozone for anti-bacterial activity on raw skins and attempted as a short-term preservation method. However, the drawback is ozone that is considered as toxic chemical. Therefore, usage of natural materials with antimicrobial activity could be useful in preservation of leather as a potential viable option.

Use of Natural Materials for short-term preservation

As such, there is no viable low salt (10%) alternative based on natural products. The use of natural eco-benign materials, with antimicrobial property such as Myrobalan in combination with common salt as low salt preservation as novel approach has been studied [30].

CONCLUSION

During leather processing, large quantities of the salt employed for short-term preservation of hides and skins, pose serious environmental concerns as well as total dissolved solids (TDS) problem in the waste-water, for which there is no viable treatment method available. Remediation measures based on separation principle end up in salt sludge, which necessitates Secured Land Fill (SLF) for disposal option, which has some concerns due to highly soluble nature of Sodium chloride. Therefore, there is a pressing need for developing alternative methods for Salt free / Less salt short term preservation of hides and skins. In this regard, it would be beneficial to review and analyze the Research and Development work on salt free alternative preservation methods as reported in literature. This review paper reviews and analyzes various alternative methods for the Salt free / Less salt short term preservation, taking in to account of both patent as well as other publications. The limitations and drawbacks associated with each alternative method have been analyzed. From the review analysis, it has been found that the use of natural eco-benign materials, with antimicrobial property could be a potential viable option for the short-term preservation of hides and skins as novel approach for sustainable development.

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