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(54) **Title:** CHROME TANNING PROCESS FOR LEATHER MAKING REUSING EXHAUST CHROME LIQUOR

(57) **Abstract:** The present invention provides a process that eliminates total usage of sodium chloride and mineral acids for pickling and ensures total utilization of tanning material through suitable process interventions for recycling without resulting in emission or discharge of process chemicals or used liquor.

CHROME TANNING PROCESS FOR LEATHER MAKING REUSING EXHAUST CHROME LIQUOR

**Field of the invention**

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The present invention relates to a zero emission chrome tanning process for leather making. More particularly, the present invention provides a pickle free chrome tanning process whereby the exhaust chrome liquor can be reused for subsequent batch of chrome tanning, thereby ensuring zero emission. This process is envisaged to have tremendous application potential in the tanning industry for making leather in eco-benign manner by way of ensuring substantial reduction of chlorides, chromium and total dissolved solids and also by affording reuse of process liquor again. The process is envisaged to enhance the economic and environmental benefits to chrome tanning.

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**Background of the invention & Description of Prior Art**

Salted hides and skins are the major raw materials for the tanning industry. In leather making process the first operation carried out is removal of the salt in the hides and skins through repeated washings. The hair and flesh are loosened by treatment with lime and sodium sulfide or enzyme and then removed using knives. The hides and skins are then agitated with acid salts like ammonium chloride for removal of residual lime. The operation is called deliming, which is usually carried out in tanning drum.

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In the hitherto known processes, the resulting delimed hides and skins are subjected to pickling using 10% salt (all percentages mentioned are on the basis of weight of hides and skins) and 1% mineral acid, in order to bring down the pH of the delimed stock, which is around 8.0 to 2.8 to 3.0 to facilitate uptake as well as penetration of chrome tanning salt (commonly known as basic chromium sulfate – BCS) in the cross section of the hides and skins to be tanned. While the penetration of BCS in hides and skins during chrome tanning is carried out at pH 2.8 to 3.0, the same is raised to 3.8 to 4.0 for fixation, which is known as basification in the industry. Alkaline salts of weak

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organic acids which are normally referred to as masking salts are added during chrome tanning process to prevent surface fixation of chromium in hides and skins.

The major limitation associated with the conventional chrome tanning processes is the generation of effluents with significant quantities of total dissolved solids due to lowering and raising of pH, chlorides and unfixed chromium. In fact, pickling and chrome tanning contribute significantly for total dissolved solids in the effluent during chrome tanning. Presence of large quantities of total dissolved solids in effluent makes the treatment of tannery effluents a cost ineffective proposal. Till date, no viable and cost effective solution is available for secured treatment of total dissolved solids. Minimizing or eliminating total dissolved solids in the effluents has been a topic of research interest for quite sometime.

Gupta et al. (Journal of Indian Leather Technologists Association, 41,24-26,1992) developed a pickle free alum – chrome combination tanning system using only 2% of salt thereby reducing use of salt to an extent of 8%. However, use of aluminium in the system impairs the feel and softness of the leathers. Further, the addition of salt is not eliminated completely. Our co pending Indian Patent application No 177 Del 2002 and US Patent 7,063,728 describe an improved process for making chrome tanned leathers whereby a mixture of conventional tanning salt and alkali metal salt is used at a pH in the range of 5.5. The method involved use of alkali dissolved in water and added in feeds of equal installments to attain a pH of 4.0 – 4.2 for completion of tanning wherein the acid liberated during hydrolysis of chromium is neutralized. However, the alkali requirements vary depending up on hydrolysis of chrome salt. Such variations are likely to result in either excess alkali or insufficient alkali at any point of time since alkali is added in equal quantities. These variations can affect the physical properties and surface characteristics of the leather adversely.

Therefore, keeping the prior art in purview it may be summarized that pickling, an important pre-tanning step practiced in the conventional chrome tanning process of leather making, involves use of significant amount of common salt,

which is largely responsible for generating high TDS (Total Dissolved Solids) content of the emanating effluent. Keeping in mind the environmental alertness, it is necessary to check the TDS level. Therefore, the inventors of the present invention realized that there exists a dire need to provide a pickle free chrome tanning process to control the TDS level of the chrome tanning liquor and wherein the spent liquor may also be reused for tanning the next batch of leather processing.

### **Objects of the Invention**

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The main objective of the present invention is thus to provide a zero emission chrome tanning process, which obviates the limitations as stated above

Another objective of the present invention is to provide a process for chrome tanning without resorting to pickling.

15 Yet another objective of the present invention is to provide a process without leading to any emission.

Still another objective of the present invention is to provide a process that results in total elimination of NaCl in processing, thereby avoiding the TDS problems altogether leading to an eco-benign option of leather making.

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### **Summary of the Invention**

The present invention relates to a process for treating the delimed hides & skins with specific combination of tanning salt and alkaline salts without affecting the tanning potency of the tanning salt and subsequent pH adjustment of the hides and skins with water only, thereby eliminating pickling operation and use of alkali for basification. The liquor is reused for tanning the next batch of leather processing.

30 Accordingly, the present invention provides for a zero emission chrome tanning process for leather making, wherein the steps comprising:

- [a] treating delimed hides and skins with 7.5 –12.0% w/w, of a mixture of basic chromium sulfate, alkali earth metal oxide and alkali metal salt of organic acid having carbon chain of length not

more than three in the ratio 10:0.25:0.88 to 10:0.38:1.25, preferably under agitation, at a pH in the range of 5-5.5 for a period of not less than 2 hrs to obtain hides/skins incorporated with chrome salt in the cross section;

5 [b] adjusting the pH of the treated hides/skins as obtained in step (a) in the range of 4-4.2 by controlled addition of water to obtain chrome tanned leather and spent chrome tan liquor;

[c] separating the spent chrome tan liquor as obtained in step (b) by known methods and using for pH adjustment in subsequent  
10 batch of chrome tanning to ensure zero emission in the chrome tanning process.

In an embodiment of the present invention, the proportion of alkali earth metal oxide and basic chromium sulfate used may be in the range of 1:26 to 1:40.

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In another embodiment of the present invention, the alkali earth metal oxide used may be selected from CaO, MgO.

In yet another embodiment of the present invention, the proportion of alkali metal salt of organic acid and basic chromium sulfate used may be in the  
20 range of 1:8 to 2:23.

In still another embodiment of the present invention, the alkali metal salt of organic acid used may be selected from sodium formate, sodium acetate,  
25 sodium citrate, potassium formate, potassium acetate.

In yet another embodiment of the present invention, known method of separation may be such as decanting, sieving.

30 In still another embodiment the present invention provides a process for conditioning delimed hides and skins to a pH in the range of 5-5.5 by conventional method followed by treatment with 7.5 –12.0% w/w, of a mixture of basic chromium sulfate, alkali earth metal oxide and alkali metal salt of organic acid having carbon chain of length not more than three in the ratio

10:0.25:0.88 to 10:0.38:1.25 preferably under agitation, for a period not less than 2 Hrs and subsequent adjustment of pH in the range of 4 - 4.2 by controlled addition of water to complete chrome tanning. The used process liquor is reused in the next batch of tanning.

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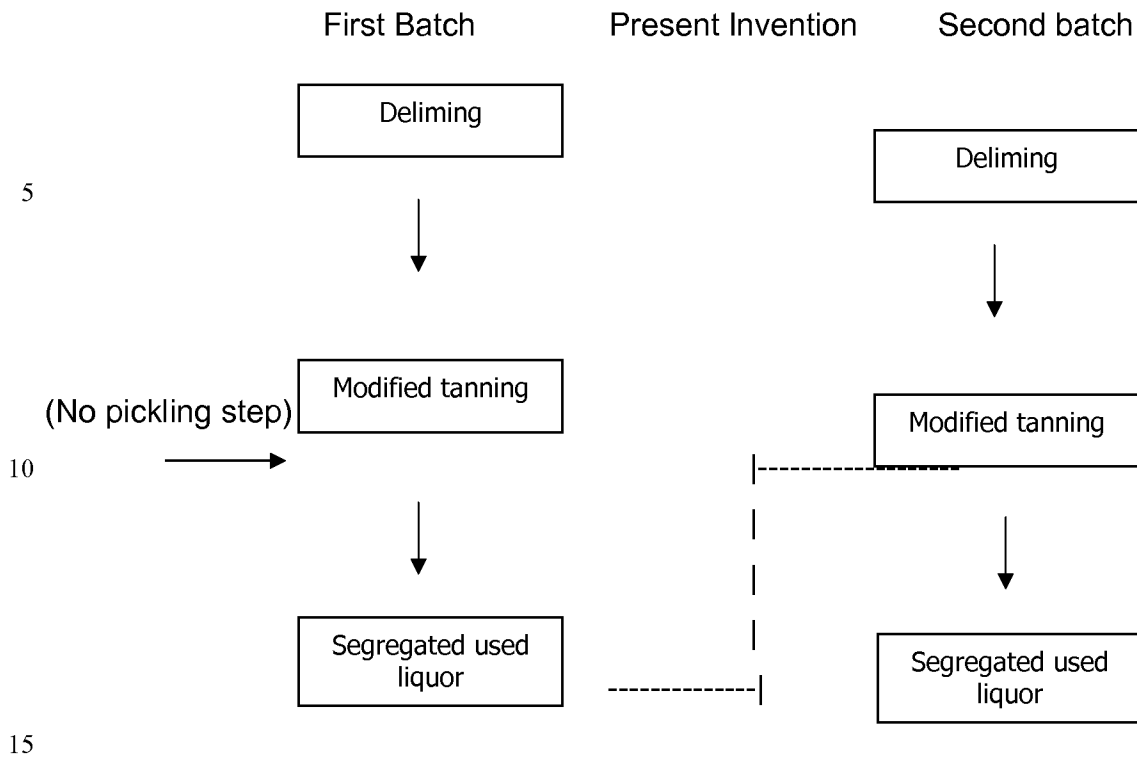
### **Detailed description of the invention**

The delimed hides and skins are conditioned to a pH in the range of 5-5.5 by conventional method. Basic chromium sulfate is mixed with alkali earth metal oxide and alkali metal salt of organic acid having carbon chain of length not more than three in a ratio of 10:0.25:0.88 to 10:0.38:1.25 and the conditioned hides and skins are treated with 7.5 –12.0% w/w of this mixture under agitation for a period not less than 2 Hrs without addition of water. The process enables penetration of tanning salt in the cross section of the hides and skins. This is ensured by checking the cross section that exhibits blue colouration. The pH is then adjusted in the range of 4-4.2 by controlled addition of not less than 40% w/w of water to complete chrome tanning process. The spent tan liquor is then segregated by known method for reuse in subsequent batch. This ensures a chrome tanning process with zero emission.

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The inventive step of the present invention lies in treating hides and skins under processing at a pH range of 5-5.5 with basic chromium sulfate along with alkali earth metal and alkali metal salt of organic acid without addition of water, thereby avoiding the conventional pickling operation and subsequently adjusting the pH with regulated addition of water only thereby eliminating alkali additions for completing chrome tanning process, which results in minimum chromium in process liquor affording direct reuse of this liquor in subsequent batch for pH adjustment. A brief overview of the process is presented in the following chart:

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The following examples are given by way of illustration and therefore should not be construed to limit the scope of the present invention.

**Example 1**

10 delimed goat skins weighing 10 kilos were taken in a drum. 30 gms of formic acid dissolved in 300ml of water was added to drum and the skins were agitated for a period of 20 minutes to attain a pH of 5.5. The skins were then agitated with 700 gms basic chromium sulfate, 17.5 gms of MgO and 61.25 gms of sodium formate for a period of 2 hours. The cross section of the skin was checked and found to be blue in color indicating complete penetration of chromium. The pH of the skins were then adjusted to 4.2 by adding 4 L of water to the drum, where in the skins were agitated continuously, in 16 equal installments over a period of 80 minutes to complete chrome tanning. The used liquor was quantitatively collected (4 L) and reused for adjusting the pH of the second batch of 10 delimed goat skins weighing 10 kilos.

**Example 2**

10 delimed sheep skins weighing 8 kilos were taken in a drum. 30 gms of acetic acid dissolved in 300ml of water was then added to drum and the skins were agitated for a period of 15 minutes to attain a pH of 5.0. The skins were  
5 then agitated with 800 gms basic chromium sulfate, 30 gms of CaO and 100 gms of sodium acetate for a period of 2 hours. The cross section of the skin was checked and found to be blue in color indicating complete penetration of chromium. The pH of the skins were adjusted to 4.0 by adding to drum 3.2 L  
10 of water, in 8 equal installments over a period of 80 minutes to complete chrome tanning. The used liquor was quantitatively collected (3.2 L) and reused for adjusting the pH of the second batch of 10 delimed sheep skins weighing 8 kilos.

**Example 3**

15 10 delimed cow hides weighing 100 kilos were taken in a drum. 500 gms of lactic acid dissolved in 5.0 L of water was then added to the drum and the hides were agitated for a period of 30 minutes to attain a pH of 5.2. The hides were then agitated with 10.0 kgs of basic chromium sulfate, 300 gms of MgO and 800 gms of sodium citrate for a period of 3 hours. The cross section of the  
20 hides were checked and found to be blue in color indicating complete penetration of chromium. The pH of the hides were adjusted to 4.0 by adding to drum 45 L of water, in 10 equal installments over a period of 100 minutes to complete chrome tanning. The used liquor was quantitatively collected (45 L) and reused for adjusting the pH of the second batch of 10 delimed cow hides  
25 weighing 100 kilos.

**Advantages of the Invention:**

- It is a versatile process, which is applicable to both hides and skins.
- Complete elimination of discharge of process liquor is effected by this  
30 process.
- It ensures that uneven stains do not appear on the leather.
- The process is cost effective and environmentally friendly.

**We claim:**

1. A zero emission chrome tanning process for leather making, wherein the steps comprising:
  - [a] treating delimed hides and skins with 7.5 –12.0% w/w, of a mixture of basic chromium sulfate, alkali earth metal oxide and alkali metal salt of organic acid having carbon chain of length not more than three in the ratio 10:0.25:0.88 to 10:0.38:1.25, preferably under agitation, at a pH in the range of 5-5.5 for a period of not less than 2 hrs to obtain hides/skins incorporated with chrome salt in the cross section;
  - [b] adjusting the pH of the treated hides/skins as obtained in step (a) in the range of 4-4.2 by controlled addition of water to obtain chrome tanned leather and spent chrome tan liquor;
  - [c] separating the spent chrome tan liquor as obtained in step (b) by known methods and using for pH adjustment in subsequent batch of chrome tanning to ensure zero emission in the chrome tanning process.
2. A process as claimed in claim 1, wherein the proportion of basic chromium sulfate and alkali earth metal oxide used is in the range of 26:1 to 40:1.
3. A process as claimed in claim 1, wherein the alkali earth metal oxide used is selected from CaO and MgO.

4. A process as claimed in claim 1, wherein the proportion of basic chromium sulfate and alkali metal salt of organic acid used is in the range of 8:1 to 23:2.
- 5 5. A process as claimed in claim 1, wherein the alkali metal salt of organic acid used is selected from the group consisting of sodium formate, sodium acetate, sodium citrate, potassium formate and potassium acetate.
- 10 6. A process as claimed in claim 1, wherein the separation process is such as decanting, sieving.

# INTERNATIONAL SEARCH REPORT

International application No <b>PCT/IB2012/050956</b>
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<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. C14C3/06                      C14C3/32 ADD.				
According to International Patent Classification (IPC) or to both national classification and IPC				
<b>B. FIELDS SEARCHED</b>				
Minimum documentation searched (classification system followed by classification symbols) C14C				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  EPO-Internal, WPI Data				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	US 2004/031106 A1 (SUNDAR VICTOR JOHN [IN] ET AL) 19 February 2004 (2004-02-19) cited in the application paragraphs [0002] - [0004], [0008], [0015], [0021] - [0048], [0050] - [0053]; examples 1-4  -----	1-6		
A	US 4 211 529 A (KOMAREK ERNST [DE] ET AL) 8 July 1980 (1980-07-08) column 1, line 45 - column 2, line 45 example 11  -----	1-6		
A	DE 36 36 002 A1 (ROEHM GMBH [DE]) 28 April 1988 (1988-04-28) page 3, line 14 - page 11, line 12; example 1  -----	1-6		
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.				
* Special categories of cited documents :  <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;">                     "A" document defining the general state of the art which is not considered to be of particular relevance                      "E" earlier application or patent but published on or after the international filing date                      "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)                      "O" document referring to an oral disclosure, use, exhibition or other means                      "P" document published prior to the international filing date but later than the priority date claimed                 </td> <td style="width: 50%; border: none; vertical-align: top;">                     "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention                      "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone                      "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art                      "&amp;" document member of the same patent family                 </td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family			
Date of the actual completion of the international search	Date of mailing of the international search report			
5 July 2012	16/07/2012			
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Neugebauer, Ute			

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2012/050956

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2004/087967 A1 (TFL LEDERTECHNICK GMBH [DE]; KETTERMANN JOAO AUGUSTO [BR]; TRIPOT LAUR) 14 October 2004 (2004-10-14) page 1 - page 1, paragraph 1 page 2, paragraph 3 - page 5, paragraph 4 examples A1,B1 -----	1-6

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Information on patent family members

International application No PCT/IB2012/050956
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