# REDUCTION OF POLLUTANTS IN THE TANNING INDUSTRY USING THE REVERSE TANNING METHOD AGAINST THE PHYSICAL PROPERTIES OF LEATHER

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**REDUCTION OF POLLUTANTS IN THE TANNING INDUSTRY USING THE REVERSE TANNING METHOD AGAINST THE PHYSICAL PROPERTIES OF LEATHER**

ABSTRACT. This study aims to tan the skin with reverse tanning based on the order of pH, thereby reducing the use of chemicals and water due to the pH regulation process. The reverse tanning method will result in a faster tanning process and reduce the use of many chemicals, so that the pollutant load released from the tanning process will be much reduced. Conventional leather tanning is carried out through many processes starting from the BHO (Beam House Operation) process, tanning, post-tanning, and finishing; this process is carried out through a 14-15 step process that produces a large number of pollutants. This is because in conventional leather processing a lot of pH adjustment processes are carried out that go back and forth. In this study the leather processing steps were ordered based on the pH of the tanning process, the chemicals and the pH of the process were regulated by the sequence of the process steps to avoid some repeated acidification and basification/neutralization as in conventional leather processing. The process begins with soaking, liming, fleshing, deliming, tanning, dyeing, fatliquoring, and chrome tanning. This process begins with an alkaline pH of 11 and ends with an acidic pH of 3.8. Chrome tanning is done with variations in the amount of chrome of 2%, 3%, 4%. The results showed that leather with 4% chromium produced the highest Ts of 103 °C, tensile strength of 39.86 N, tearing strength of 13.19 N/mm, seam strength of 12.8 N/mm, elongation of 46.87%, Cr content (VI) 1.68 ppm. These results have met the standard ISO/TR 20879:2007 Footwear. The reverse tanning process with a process from high to low pH without adjusting the pH back and forth by adding solutions and salts means reducing liquid waste in the leather tanning process. So, this process can reduce the amount of liquid waste or pollutants.

KEY WORDS: reverse tanning, leather processing, chrome tanning, shrinkage temperature

**REDUCEREA POLUANȚILOR DIN INDUSTRIA DE PIELĂRIE UTILIZÂND METODA TĂBĂCIRII INVERSE ȘI INFLUENȚA ACESTEIA ASUPRA PROPRIETĂȚILOR FIZICE ALE PIELII**

REZUMAT. Acest studiu își propune tăbăcirea pielii prin procesul de tăbăcire inversă în funcție de ordinea pH-ului, reducând astfel utilizarea substanțelor chimice și a apei datorită procesului de reglare a pH-ului. Metoda de tăbăcire inversă va avea ca rezultat un proces de tăbăcire mai rapid și va reduce utilizarea multor substanțe chimice, astfel încât încărcătura poluantă eliberată din procesul de tăbăcire va fi mult redusă. Tăbăcirea convențională a pielii se realizează prin multe operațiuni pornind de la cele umede, tăbăcire, post-tăbăcire și finisare, acest proces fiind realizat în 14-15 etape care produc o cantitate mare de poluanți. Acest lucru se datorează faptului că în prelucrarea convențională a pielii sunt efectuate o mulțime de procese de ajustare a pH-ului în ambele sensuri. În acest studiu, etapele de prelucrare a pielii au fost ordonate în funcție de pH-ul procesului de tăbăcire, substanțele chimice și pH-ul procesului a fost reglate de succesiunea etapelor pentru a evita unele acidificări și alcalinizări/neutralizări repetate, așa cum se întâmplă la prelucrarea convențională a pielii. Procesul implică înmuierea, cenușărirea, șeruirea, decalcifierea, tăbăcirea, vopsirea, ungerea și tăbăcirea în crom. Acest proces începe cu un pH alcalin de 11 și se termină cu un pH acid de 3,8. Tăbăcirea în crom se face cu variații ale cantității de crom de 2%, 3%, 4%. Rezultatele au arătat că pielea cu 4% crom a generat cea mai mare valoare a Ts de 103 °C, rezistență la rupere de 39,86 N, rezistență la sfâșiere de 13,19 N/mm, rezistența cusăturii de 12,8 N/mm, alungire de 46,87%, conținut de Cr (VI) 1,68 ppm. Aceste rezultate au îndeplinit standardul ISO/TR 20879:2007 Încălțăminte. Procesul de tăbăcire inversă începând de la un pH ridicat până la un pH scăzut fără ajustarea pH-ului prin adăugarea de soluții și săruri înseamnă reducerea deșeurilor lichide în procesul de tăbăcire a pielii. Deci, acest proces poate reduce cantitatea de deșeuri lichide sau poluanți.

CUVINTE CHEIE: tăbăcire inversă, prelucrarea pielii, tăbăcire în crom, temperatură de contracție

**RÉDUCTION DES POLLUANTS DANS L'INDUSTRIE DU CUIR EN UTILISANT LA MÉTHODE DE TANNAGE INVERSE ET SON INFLUENCE SUR LES PROPRIÉTÉS PHYSIQUES DU CUIR**

RÉSUMÉ. Cette étude vise à tanner la peau en utilisant un tannage inverse basé sur l'ordre du pH, réduisant ainsi l'utilisation de produits chimiques et d'eau en raison du processus de régulation du pH. La méthode de tannage inverse entraînera un processus de tannage plus rapide et réduira l'utilisation de nombreux produits chimiques, de sorte que la charge polluante libérée par le processus de tannage sera considérablement réduite. Le tannage conventionnel du cuir est réalisé à travers de nombreux processus à partir des opérations de rivière, tannage, post-tannage et finition, ce processus est réalisé en 14-15 étapes qui produisent une grande quantité de polluants. En effet, dans le traitement conventionnel du cuir, de nombreux processus d'ajustement du pH sont effectués dans les deux sens. Dans cette étude, les étapes de traitement du cuir ont été ordonnées en fonction du pH du processus de tannage, les produits chimiques et le pH du processus ont été régulés par la séquence des étapes pour éviter une acidification et une basification/neutralisation répétées comme dans le traitement conventionnel du cuir. Le processus commence par le trempage, le pelanage, l'écharnage, le déchaulage, le tannage, la teinture, la nourriture et le tannage au chrome. Ce processus commence avec un pH alcalin de 11 et se termine avec un pH acide de 3,8. Le tannage au chrome se fait avec des variations dans la quantité de chrome de 2%, 3%, 4%. Les résultats ont montré que le cuir avec 4 % de chrome

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produisait la Ts la plus élevée de 103 °C, une résistance à la traction de 39,86 N, une résistance à la déchirure de 13,19 N/mm, une résistance des coutures de 12,8 N/mm, un allongement de 46,87 %, une teneur en Cr (VI) de 1,68 ppm. Ces résultats sont conformes à la norme ISO/TR 20879:2007 Chaussures. Le processus de tannage inverse avec un pH élevé à faible sans ajuster le pH dans les deux sens en ajoutant des solutions et des sels signifie la réduction des déchets liquides dans le processus de tannage du cuir. Ainsi, ce processus peut réduire la quantité de déchets liquides ou de polluants.
MOTS CLÉS : tannage inverse, traitement du cuir, tannage au chrome, température de retrait

## INTRODUCTION

Leather is a waste from the meat industry which will be damaged by the autolysis process if it is not immediately preserved [1]. Raw hide in order to be used must be processed through a tanning process. Tanning is a chemical process that reacts skin collagen with chemicals so that cross-linking occurs, resulting in a tanned leather that is stable and resistant to external influences [2].

Chrome tanning is the most widely used tanning in the leather industry, as it can provide leather with a comfortable feel and high hydrothermal stability. In addition, compared to chrome-free tanning, chrome tanning is more suitable for the production of various types of leather. Crust skin from chromium tanning has better compatibility/compatibility with chemical retanning and fatliquoring, in other words, it is easy to retan and fatliquor without causing negative effects [3]. Conventional chrome tanning has the characteristics of releasing excessive chromium into the waste and abundant chromium shavings. The release of chromium into the waste is caused by imperfect absorption of chromium powder, namely 40%-70% absorbed and the release of free/unbound and unstable chromium from the skin during post tanning processes such as rewetting, retanning, neutralizing, dyeing and fatliquoring processes done after chrome tanning to improve leather grip and feel, as well as leather coloring. It is expected that the addition of chromium at the end of the process can reduce the release of chromium to waste.

Conventional leather processing is usually carried out through many processes to remove various biological, inorganic, and organic materials. The process starts from BHO, tanning, post-tanning, and finishing, this leather processing is carried out up to 4-15 steps of the process which produces a large amount of water pollutants and chemicals. This is because conventional leather processing is mostly done by adjusting the pH that goes back and forth. In this study the leather processing steps were sequenced to overcome the problems associated with the conventional method, wherein the skin charge, chemical and process pH were set for reversal of the process steps to avoid some repeated acidification and basification/neutralization as in conventional leather processing. In this study, it is expected that there will be savings in chemicals, water and time so that the tanning process is more efficient.

The conventional method of making leather goes through 14-15 steps consisting of soaking, liming, reliming, deliming, removing fat, protein scraping, acidification, tanning, basification, rechroming, neutralization, washing, retanning, dyeing, fatliquoring, and fixation. This conventional tanning produces a large amount of liquid waste, about 30-40 $m^3$ per 1 ton of raw hide raw material, in which the wastewater contains pollutants such as BOD, COD, TDS, sulfides, chlorides, sulfates, chromium, total ammonia, total nitrogen [4].

The increase in pollutants in conventional processes is mainly due to the fact that the leather processing technique uses a “do-undo” process scheme such as swell-deswell (liming-deliming), pickle-depickle (pickling-basification), rechroming-basification (acidification-basification), and neutralization-fixation (basification-acidification) [5]. In other words, conventional methods in skin processing cause the pH range of the process from start to finish to be wide and varied [6]. Such changes in pH require the repeated use of large amounts of acids and bases, resulting in the production of salts of calcium, sodium, and chromium ions, as well as increasing COD, TDS, chlorides, sulfates, and other minerals in tannery wastewater [1].

The post tanning process goes through 7-8 main steps consisting of rechroming, basification, neutralization, washing, retanning, basic coloring, oiling, and fixation. This post-tanning process is in the pH range of 4.0-6.5 and contains many chemicals, thus contributing significantly to TDS, COD, and heavy metal pollution [3]. Several attempts have been made to fabricate leather processing steps with clean technology [7, 8]. However, these efforts are specific to each operating unit. Therefore, the application of all advanced technologies and eco-friendly chemicals and machine modifications should be carried out for the development of integrated leather processing methods and revamping of the process sequence. Very little effort has been made to change the whole or part of the leather processing step. Thanikaivelan *et al*. tried to process skin in a narrow pH range of 4 to 8.0 [1, 9]. Later, a three-step tanning process was developed which involves enzymatic dehairing, fiber opening using enzymes or alkali, and chrome tanning without acidification at pH 8.0 [10, 11]. An integrated one-step wet finishing process has been developed [12, 13]. Furthermore, process integration has been attempted by combining tanning and post-tanning in one process [14].

This research as a novelty step will be made an effort to reverse the steps of the conventional tanning process, by treating the leather for the post tanning process (retanning, dyeing and fatliquoring) carried out in the pre tanning process (beam house) with no neutralization process, followed by chrome tanning at pH 3.5 – 4.0 without pickle process [9].

## EXPERIMENTAL

### Materials and Method

#### *Instruments*

Drum process, pH paper, glass tools. The resulting leather is tested according to ISO/TR 20879:2007 footwear standards, covering tensile strength, tear strength, seam strength, elongation, remaining Cr (VI), and shrinkage temperature (Ts).

#### *Materials*

The materials used in this research are salt-resistant leather, water, surfactant, $Na_2S$, lime, $NH_4Cl$, bating agent, degreasing agent, glutaraldehyde, syntan, dyestuff, fatliquour oil, synthetic oil, HCOOH, chrome sulfate powder.

#### *Method*

Salt-preserved goat skin is processed conventionally by soaking, liming, fleshing, deliming and then processed by retanning, dyeing, and fatliquoring. Finally it is tanned using chrome tanning agent. Tests were carried out for physical and chemical test parameters. The reverse tanning process in this study can be seen in Table 1.

Table 1: Reverse tanning process

| No. | Process | Chemicals | % | Time | Process control |
|---|---|---|---|---|---|
| 1 | Salt-preserved goat skin<br>Weighing | | | | |
| 2 | Washing and Soaking | Water | 500 | | |
| | | Wetting agent | 0.5 | 60' | Drain, wash<br>2-4 rpm<br>pH 7 |
| 3 | Liming | Water | 150 | | 2-4 rpm |
| | | $Na_2S$ | 2.5 | 30' | pH 11-12 |
| | | Water | 50 | | |
| | | Lime | 6 | 30 | |
| | | Water | 50 | 30' | |
| | | Water | 50 | 30'<br>30' run<br>15' res | |

| No. | Process | Chemicals | % | Time | Process control |
|---|---|---|---|---|---|
| 4 | Fleshing | | | | |
| 5 | Deliming | Water | 200 | | 6-8 rpm |
| | | $NH_4Cl$ | 2 | | |
| | | Bating agent | 1 | | |
| | | Degreasing agent | 1 | 90' | Check pH |
| | | HCOOH | 0.5 | 30' | pH 6,7,8 |
| | | Washing | | | |
| 6 | Retanning, dyeing, and fatliquoring | Water | 100 | | 10-12 rpm |
| | | Syntan | 5 | 30 | |
| | | Glutaraldehyde | 4 | 30 | |
| | | Dyestuff | 2 | 60 | |
| | | Sulfited oil | 5 | 15 | |
| | | Synthetic oil | 3 | 60 | |
| 7 | Fixation | HCOOH | 0.5 – 1 | 30' | 10-12 rpm<br>pH 3.5-4 |
| 8 | Tanning | Chrome sulphate | Variation<br>2, 3, 4 | 90' | 10-12 rpm |
| | | | | 180' | Drain, hanging, drying |

## RESULTS AND DISCUSSIONS

This research of reverse tanning by treating the leather from washing after deliming, retanning, dyeing, fatliquoring, fixation, and tanning. In the reverse tanning process, it only goes through 8 stages from high pH 11-13 to pH 3.5-4 at the end of the process. The resulting leather is tested according to ISO/TR 20879:2007 footwear standards. Variations in the amount of chromium in reverse tanning include the amount of chromium 2%, 3%, 4% of the weight of the skin. Variations in the amount of chromium can be seen in Table 2.

Table 2: Variations in the amount of chromium, pH of deliming and product code

| Variations of chromium (%) | pH of deliming 6 | 7 | 8 |
|---|---|---|---|
| 2 | A | D | G |
| 3 | B | E | H |
| 4 | C | F | I |

The test results of leather from process reverse tanning with several treatments are carried out were physical and chemical tests according to ISO/TR 20879:2007 for Footwear.

Table 3: Results of leather physical and chemical test results of reverse tanning

| No. | Various Test | Test Results A | B | C | D | E | F | G | H | I | Remark |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Tear Strength (N) (ISO 17696:20011) | 51.74 | 37.80 | 25.97 | 44.77 | 41.90 | 45.54 | 48.06 | 32.27 | 39.86 | Min. 30 |
| 2 | Colour Fastness (ISO 17700:2011) | | | | | | | | | | |
| | Wet (20 cycles) | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | Min. 2 |
| | Greyscale | | | | | | | | | | |
| | Dry (100 cycles) | 4/5 | 4/5 | 4/5 | 4/5 | 4/5 | 4/5 | 4/5 | 4/5 | 4/5 | Min. 2 |
| 3 | Lastability (mm) (ISO 17693:2011) | 23.50 | 13.26 | 17.07 | 19.80 | 15.0 | 13.18 | 21.18 | 17.70 | 12.28 | Min. 6 |
| 4 | Seam Strength (N/mm) (ISO 17697:2011) | 5.55 | 1.77 | 4.90 | 5.67 | 4.29 | 4.26 | 5.14 | 2.55 | 4.34 | Min. 3 |
| 5 | Breaking strength (N/mm) (ISO 17706:2011) | 11.18 | 14.17 | 12.13 | 13.30 | 13.02 | 17.40 | 12.82 | 8.99 | 13.19 | Min. 10 |
| 6 | Elongation (along) (%) (ISO 17706:2011) | 18.72 | 46.82 | 44.50 | 23.05 | 53.36 | 51.10 | 48.10 | 19.10 | 46.87 | Min. 7 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 7 | Chromium (6) content (mg/kg) (ISO 17075:2007) | 0.34 | 0.34 | 0.42 | 0.25 | 1.57 | 1.71 | 1.74 | 2.13 | 1.68 | Max. 3 |
| 8 | Shrinkage Temperature (Ts) (°C) SNI 06-7127-2005 | 86.9 | 92.5 | 98.8 | 87.7 | 95.3 | 100.1 | 90.7 | 96.9 | 103.3 | Min 100°C |

The thickness, direction of the collagen fibers, and the angle of the collagen fibers to the grain layer affect the tear strength of tanned leather, the higher the tear strength, the better the resulting quality [15]. The tear strength can be increased by controlling the percentage (amount) of the bating material used and the time of the protein scraping process (bating). The use of too much batting material and too long batting processing time will result in low tear strength.

On leather code B and H the sewing strength test does not meet the requirements of ISO/TR 20879:2007 Footwear – Performance requirements for components footwear – Uppers. The strength of the suture is influenced by the thickness of the skin, the content and density of the collagen protein, the angle of the interwoven collagen fibers and the thickness of the corium. So that the protein erosion process will greatly affect the sewing strength of the leather, the greater the percentage of enzymes used and the longer the protein erosion process will reduce the sewing strength of the tanned leather.

Tensile strength is the maximum force required to pull the skin to break, expressed in kg/cm$^2$ or N/mm$^2$. Tensile strength is one of the important parameters that becomes a benchmark for the quality of tanned leather because it can describe the strength of the bond between the collagen fibers that make up the skin and the tanning agent. A good tanning process will produce leather with high tensile strength. Tensile strength in its application is very important, especially in the leather product/goods industry. The tensile strength of the leather that is less than the requirement will cause the leather to break or crack easily. Tensile strength testing is generally carried out to determine the mechanical properties of a material. For treatment with variation code H, the tensile strength test does not meet the requirements of ISO/TR 20879:2007 Footwear – Performance requirements for components footwear – Uppers. Factors that can affect the tensile strength are the quality of raw leather, leather preservation methods, and processes during tanning, such as liming, bating, oiling, and stretching [16]. Mann (1981) said that the physical properties of the skin are influenced by the structure of the skin tissue, namely the collagen bundles that make up the skin that are irregularly woven with each other, branching in all directions [17]. The angle formed by the webbing of the beam determines the high and low tensile strength, at a webbing angle of less than 450, the leather will have a high tensile strength and vice versa if the angle formed by the collagen fibers is more than 450 then the resulting tensile strength will be higher. A small collagen bundle angle will produce a leather that is strong and less elastic, but softer than leather with a larger collagen bundle angle. The results of the shrinkage temperature test showed that the lowest shrinkage temperature was in variation A, which was 86°C and the highest was in variation I, which was 103.3°C, this indicates that the higher the addition of chromium, the more cross-linking occurs so that the chemical stability of the collagen structure increases. The increase in shrinkage temperature was caused by the stabilization of the chemical reaction of the collagen structure with the equalizer [18].

Leather elongation is an increase in the length of the leather at the time it is stretched to break divided by its original length, expressed in percent. Elongation shows the elongation of the leather, the longer the size of the leather at the time of breaking, the greater the value of the elongation strength, which indicates that the quality of the elongation strength is good. However, the stretch is limited to a certain value because if it is too stretchy the leather will not be able to maintain its shape when leather products are made. Of all the variations in the research, it meets the requirements of ISO/TR 20879:2007 for Footwear, namely a minimum of 7% for length and 15% for across. In order to maintain the elongation value at a certain value, the inner coating material is usually added according to the desired elongation.

The skin shrinkage temperature is the temperature reached when the skin shrinks to a maximum of 0.3% of the initial length, if the skin is heated slowly in a heating medium, (SNI 06-7127-2005: Test Method for Tanned Skin Shrinkage Temperature). One of the parameters that determine skin maturity is to know the shrinkage temperature. The shrinkage temperature is the temperature at which the skin shrinks due to the breaking of the cross-links between the leather and the tanning agent due to the influence of heating. Ripe skin will have a higher number of cross-links than unripe skin, so it is more capable and resistant to physical forces that attack it, including boiling water [19]. Each type of tannery produces leather with different heat resistance, this is due to the different types of chemical bonds formed between the tanning agent and the leather.

The higher the percentage of addition of tanning material, the higher the shrinkage temperature, this indicates that the tanning material that enters and binds to the skin forms more compact fiber bonds, so that the resistance to heat increases, the shrinkage temperature is the temperature at which the collagen structure shrinks. Shrinkage occurs due to folding of the polypeptide chain due to the breaking of the strength of the woven fibers by extreme conditions (e.g. heating) [20]. Shrinkage temperature is a temperature that can cause damage and tends to cause a decrease in the binding capacity of substances contained in proteins [21]. The shrinkage temperature is closely related to the maturity of the skin, the more skin fibers that bind to the tanning agent, the higher the maturity of the resulting skin so that the shrinkage temperature is higher. The higher the shrinkage temperature, the better the quality of the product because the skin's resistance to heat (hydrothermal) is higher.

The reverse tanning process with a process from high to low pH without adjusting the pH back and forth by adding solutions and salts means reducing liquid waste in the leather tanning process. So, this process can reduce the amount of liquid waste.

## CONCLUSIONS

The results of the study concluded that the highest shrinkage temperature was code I (reverse tanning with 4% chromium of the skin weight). Reverse tanning code I with 4% chromium of the skin weight, by process with weighing, soaking, liming, fleshing, deliming, retanning, dyeing, fatliquouring, fixation, and chrome tanning with 4% chromium. The results showed that leather with 4% chromium produced the highest Ts of 103°C, tensile strength of 39.86 N, tearing strength of 13.19 N/mm, seam strength of 12.8 N/mm, elongation of 46.87%, Cr content (VI) 1.68 ppm. These results have met the standard ISO/TR 20879:2007 Footwear.

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