Livestock and Animal Research
Accredited by Directorate General of Strengthening for Research and Development No. 10/E/KPT/2019

Open Access
Livest. Anim. Res., November 2023, 21(3): 163-169
p-ISSN 2721-5326 e-ISSN 2721-7086
https://doi.org/10.20961/lar.v21i3.66093

Original Article

Physical structure of leather tanned with aluminium as an alternative tanning agent

Emiliana Anggriyani*, Nais Pinta Adetya, Laili Rachmawati, and Nurwantoro

Department of Leather Processing Technology, Politeknik ATK Yogyakarta
*Correspondence: emiliana.anggry@gmail.com

Received: October 5th, 2022; Accepted: September 20th, 2023; Published online: November 13th, 2023

Abstract

Objective: This study aims to examine the physical structure of goat skins tanned with aluminium as an alternative tanning agent.
Methods: Twelve pieces of goat skin from the pikle breed were used in the study. Chromosal B, an aluminium tanning agent, Novaltan Al, salt (NaCl), Derminol OCS, MgO, Sodium bicarbonate, a BCG indicator, Permit MLN, and an anti-fungal are among the chemicals utilized. The approach involves tanning using chrome tanning as a control and aluminum tanning with amounts of 2%, 4%, and 6% Al_2O_3. Cross-sectional tests were used to assess the wet white leather's results, and the SEM-EDX method was used to determine the leather's composition.
Results: Leather tanned with aluminium tanning agent shows the distribution of aluminium in the skin section, the increasing use of aluminium tanning materials, the higher the aluminium content in tanned leather.
Conclusions: The presence of aluminium tanning agent in the skin indicates an interaction between the material and the skin so that it can be used as an alternative tanning agent.

Keywords: Aluminium; Free chrome; Mineral tanning agent; Physical structure

INTRODUCTION

The mineral tanning process is the tanning of leather using various tanning materials chrome, aluminium, zirconium etc. Due to cross-links with different groups, aluminium, zirconium, and titanium tanning differ from chrome tanning (covalent, ionic, hydrogen bonds). Since they create leathers with extremely distinct (and typically inferior) qualities, these tannages cannot be viewed as alternatives to chromium tanning. [1]. Various studies have been carried out to determine the quality of the leather from various tanning materials. Chrome tanner has many advantages over other tanners. To create useable leathers, chrome tanning must be combined with the extra procedures of dyeing, fatliquoring, and maybe vegetable re-tannage. High speed, low cost, light color, and great protein preservation are the primary benefits of chrome tanning. Chrome tanning rapidly took its place in the commercial world shortly after its discovery and became the most common method of tanning light leathers and shoe upper leathers [2].

On several occasions, it has been known that although the quality of leather from chrome tanneries is of the best quality, there are weaknesses in terms of waste disposal and the possibility of formation of chrome VI on the leather. High levels of excess Cr(III)-tanning products continue to pose a potential concern to the environment and are a significant contributor to the amount of persistent pollutants within the context of industrial needs [3]. Because the chemicals employed were used more thoroughly, the wastewater from the chrome-free tanning process was less polluting than the wastewater from the chrome tanning process, notably in terms of COD (around 25%) [4]. Environmental pollution with Cr (VI) poses a severe danger due to its toxicity, carcinogenicity, and mutagenicity. Chromium-containing effluents should be treated with an effective technique to meet the discharge standards before they are released into the receiving environment to prevent environmental contamination [5]. Because it creates high-quality leather with all the desired characteristics, chrome tanning technique is the most well-liked and top choice of the global leather business. Yet, due to its unfavorable consequences on the environment, human health, and other organisms, this technology is divisive [6]. The tanning chemical basic chromium sulfate (BCS), which is utilized, is not entirely absorbed by the skin and is discharged with the effluent. This contributes to a serious pollution problem. BCS is utilized in tanning, where it is changed into the purportedly cancer-causing Cr(VI) form of Cr (III) [7]. Even though the chromium in leather is Cr(III) rather than the poisonous Cr, disposing of chrome still presents some challenges (VI)[8]. Hence, more investigation is required into the use of non-chrome tanning ingredients in the tanning of leather.

The tanning process is expected to produce the best quality tanned leather. The leather produced is able to pass the test standards both by the customer, national and international standards. In supporting this, the first thing to know is the characteristics of the skin that has been tanned. It is important to know whether the chemical that is inserted is well penetrated or not, able to bind to the skin or not.

In the last several years, processes have been created to lessen or eliminate the vast amounts of chrome shavings and prevent their disposal on hazardous waste sites. This was accomplished through preparatory tanning without chrome and shrinking at a temperature suitable for flawless wet shaving. Wet white leather is the term used to describe the leather created by such a process. It is also feasible to produce wet white using goods including acrylic sulfuric acid or sodium aluminium silicate [9]. The presence of aluminium in the tannage, whether alone or in conjuction with Cr(III), confers firmness. For some application, this is desirable: a well-known example is for light weight leathers for shoe uppers, such as ladies weight calf leather, which is stiff leather capable of being shaped on the shoemaker's last [10]. The surface of aluminium-tanned leather is as smooth as woolen fabric, and it is completely white, supple, tight, bright, and flexible [11]. The distinctive qualities of aluminium and zinc salts are widely accessible, produce white leather, are less expensive, and have a smaller environmental impact. Basic aluminium sulfate-masked citrate's shrinkage temperature was discovered to be 83°C [12]. The new technology, which is not deemed harmful and is safe for both people and the environment. The method is based on a mineral tanning technique that utilizes compounds made of silicon, aluminium, and natural polycarboxylic acids [13].

MATERIALS AND METHODS

Materials

As many as 12 pieces of pickling goat skin with an area of 7 square feet and a thickness of 0.7 to 0.75 mm are used as the raw material for the leather. Novaltan Al, an aluminium tanning agent, salt (NaCl), Peramit MLN, Derminol OCS, MgO, sodium bicarbonate, a BCG indicator, and an anti-fungal are among the chemicals utilized. The equipment includes an inclined table, a trial drum, a bucket, a baumemeter, a knife, a thickness gauge, and other items.

Methods

In order to conduct the research, aluminium tanning material was used in place of chrome tanning material during the tanning procedure. Three different Al_2O_3 concentration levels 2%, 4%, and 6% were used in the tanning process, with chrome serving as a control.

Stages of the Tanning Process

Table 1 shows the steps of the tanning process using chrome tanning material. Table 2 shows the steps of the tanning process using aluminium tanner.

Table 1. Tanning process with chrome tanner

Process	Amount (%)	Chemical	Time (minutes)	Description
Wetting back	150	H_2O	30′	8°Be
	12	NaCl		
	2	Wetting agent		pH = 3.5
Drain				
Repickling	75	H_2O	15′	
	7.5	NaCl		
	0.2	HCOOH		pH = 2,8 – 3
Tanning	75	Salts water	10′	8°Be
	6	Chrome		
	2	Syntetic oil		
	0.6	MgO	300′	
	0.1	$NaHCO_3$	30′	pH = 3,8 – 4
	0.05	Anti-fungal	30′	

Table 2. Tanning process with aluminium tanner

Process	Amount (%)	Chemical	Time (minutes)	Description
Wetting back	150	H_2O	30′	8°Be
	12	NaCl		
	2	Wetting agent		pH = 3.5
Drain				
Repickling	75	H_2O	15′	
	7.5	NaCl		
	0.2	HCOOH		pH = 2,8 – 3
Tanning	75	Salts water	10′	8°Be
	2%, 4%, 6%*	Aluminium		
	2	Syntetic oil		
	0.6	MgO	300′	
	0.1	$NaHCO_3$	30′	pH = 3,8 - 4
	0.05	Anti-fungi	30′	

Cross-sectional analysis and content of tanners in leather

The EDX test (energy dispersive X-ray analysis) is then used to determine how much aluminium tanner is present in wet white leather. As well as knowing the cross-section of wet white leather using SEM (scanning electron microscopy).

RESULTS

The EDX data in Table 3 demonstrates that carbon and oxygen, which are elements frequently present in living things and are the primary constituent elements of amino acids and lipids, are the principal constituent elements of leather, whether tanned with chrome or aluminium tanners. Several substances were also found to be present in the skin, including nitrogen, sodium (Na), magnesium (Mg), sulfur (S), calcium (Ca), and chloride (Cl). These substances can also arise from chemicals used in the tanning process, including as pickling, unhairing, lime, basification, and others. These substances are naturally present in the skin as mineral salts.

Table 3. EDX results in skin with variations in aluminum concentration

Element	Crome	Al 2% (mass %)	Al 4% (mass %)	Al 6% (mass %)
C	45.43	43.17	48.86	45.02
O	22.23	34.50	25.37	32.03
Cr	0.35	-	-	-
Al	-	0.79	0.93	1.64

a. Pickle skin b. Wet white skin

Figure 1. Goat skin

Cross-section of wet white skin

Goat skin is seen in Figure 1 both before and after aluminium tanning. As seen in the image, aluminium tanning produces a flat white skin tone, sometimes known as wet white. Ammonium alum, potash-alum, and basic aluminium sulfate also are time-honored tanning substances when mixed with salts and disolved in water for immersion tans. They are widely used for fur skins and robe tanning because they leave the leather relatively soft and white [14].

SEM analysis results

SEM results on leather tanned with aluminium at a magnification of 3000 times are shown in Figure 2. Figure 2a is a control that is leather tanned using chrome tanning material, while Figure 2b is leather tanned with 2% aluminium, the skin tissue looks compact or solid, but the remaining aluminium is in the form of grains with irregular shapes on the SEM image which proves that the aluminium tanning agent is still left behind and does not enter the skin. It can be said that in addition to the penetrated tanner, it is also seen that there is a bond between the tannery material and the skin on the surface of the skin.

DISCUSSION

Skins that have been properly fleshed and dehaired are ready to put in the tanning bath. Acid tans or "pickle" tans are widely used either as complete tan, or as pretans for chrome and vegetable tanning [14]. Furthermore, pickle skin can be maintained through aluminium tanning. Collagen carboxyls and aluminium (III) interact, but the interaction is far more electrostatic than covalent. As a result, the leather still has a significant cationic character, which makes it susceptible to collapsing and adhering, yielding thin, hard leather or, in the case of pickled pelt, a tendency to create irreparable adhesions [15].

Table 3 demonstrates that the leather contains aluminium at amounts of 2%, 4%, and 6% Al_2O_3. The skin's aluminium content increases with the amount of Al_2O_3 utilized. This demonstrates that despite the increased use of Al_2O_3, the aluminium utilized in the skin is still suitable. The more aluminium that is present in the skin, the more aluminium is anticipated to be bonded to the skin's carboxylate group, improving tanning. With the penetration of the tanner, it is hoped that the temperature of the wrinkle, which is one of the signs of the tanning of the skin, can be met.

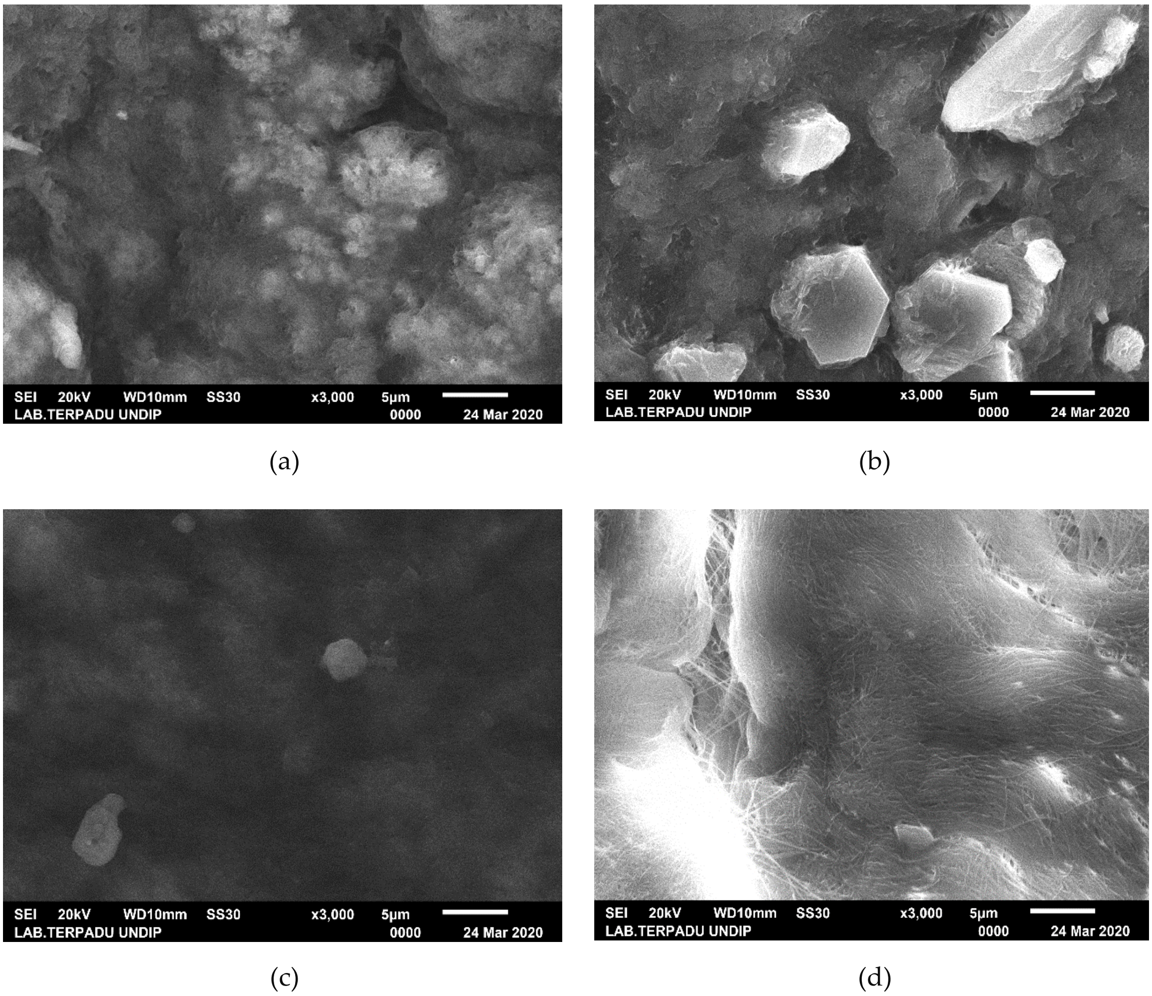

Figure 2. SEM test results, (a) control skin, chrome tanner; (b) 2% aluminium tanner; (c) aluminium tanner (4%); (d) 6% aluminium tanner

The wrinkle of pickled skin and the moist white aluminium skin are different in temperature. The temperature of the wrinkle rose after the skin had gotten tanned (shrinkage temperature). After being tanned with aluminium, pickled skin has a pH between 3.8 and 3.9. The rise in pH coincides with the temperature of the skin's wrinkles, which have gone from pickled to wet white [16]. Leathers tanned with aluminium have a lower shrinkage temperature than leathers tanned with chrome (about 80-90°C). In the case of pure aluminium tannage it is good to work with short floats in order to obtain an even absorption and bonding of the tanning agent [9]. The use of aluminium (III) tanning, which produces a nice white leather but is insufficiently water- and/or heat-resistant, is now restricted to specific applications (glace leather for gloves, the production of fur), pre-tanning, or in combination with chrome tanning to increase the uptake of chromium. To raise the temperature at which shrinkage occurs, vegetable tanning is also mixed with aluminium tanning. For additives in chrome tanning, a similar dosage or less is used; the common ratio is 6-7% mimosa tannin and 1% Al_2O_3. Aldehydes, such as (modified) glutaraldehyde, can also be mixed with aluminium salts [1].

Leather tanned using 4% aluminum (Figure 2c) shows a compact network of the skin and the tanning is even, and there is still tanner on the surface of the skin. This proves that aluminium can effectively be used for mineral tanning materials. Figure 2d shows the use of aluminium tanner by 6%, the skin is getting denser but there are still image residues in the form of dots on the SEM image, this also shows that aluminium tanner is also present on the surface of the skin. This is also shown by the EDX results of the Al component in leather at the use of concentration of Al tanner (6%) 1.64%, higher than the component Al in the skin at the concentration of Al tanner 2% and 4% (Table 3). Due to the aluminium tanning agent's comparatively low molecular weight, it may permeate the grain side and flesh side of leather, resulting in a more even dispersion of the tanning agent throughout the leather [17].

Based on the results of experiments with variations in the concentration of aluminium tanner, it was found that the higher the concentration of aluminium salts, the higher the concentration of aluminium in the skin. This is because the more aluminium salts are used, the more aluminium can be bound to the carboxylate groups in the skin collagen protein. It is feared that aluminium present in the collagen structure but not chemically bonded to the carboxylate group of the collagen protein will occur if the tanning substance is used in excess (appears as aluminium dissolved in the skin) [18]. The use of aluminium tanner is expected to produce leather that is more environmentally friendly. Many advantages of the cleaner technologies include enhanced labor productivity, consistent material quality, and a stronger global reputation. Also, the local residents and employees of the beneficiary tannery units will receive benefits. Other advantages include a decrease in air and water pollution, improved working conditions, and increased occupational safety [19].

Based on Table 3, aluminium tanners can penetrate into the skin and are able to show cross-links with skin collagen. In the process of using aluminium, it is quite a bit around 2-6% aluminium, while chrome tanning materials that are starting to be limited can use 6-8% chrome. Therefore, considering that chrome tanning materials are starting to be limited due to the possibility of the emergence of carcinogenic Cr (VI), it is still necessary to consider alternative combinations of using chrome and aluminium as leather tanning materials. In the business, chrome tanning is the most used tanning method because to its effectiveness, affordability, and environmental friendliness. The most recent technology allows tanneries to reduce the chromium content of their effluents to below the permitted limit values, but only at great expense. On the other hand, chrome tanning produces leathers of such great quality and variety that no other tanning method has yet been discovered that offers the same level of universality, quality, and stylistic diversity. The air and water are contaminated by the chromium and other inorganic contaminants. There are times when the chrome tanned leather produces dangerous compounds that are detrimental to humans and the environment [20]. In this instance, wet-white (chrome-free) tanning has received more attention in the creation of Ecoleather in order to replace or scale back on conventional chrome tanning [21].

CONCLUSION

Aluminium tanning agent is proven to be able to be used for tanning leather, with the penetration of the tanner into the skin. The higher the Al_2O_3 used, the higher the aluminium content in the skin. The presence of aluminium tanning agent in the skin indicates an interaction between the material and the skin so that it can be used as an alternative tanning agent (wet white skin).

CONFLICT OF INTEREST

The author declares no conflict of interest with any financial organization regarding the material discussed in the manuscript. The funder had no role in the research design; in the collection, analysis, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

ACKNOWLEDGMENT

This works has been financed by Politeknik ATK Yogyakarta.

REFERENCES

1. Buljan, J. and I. Kráľ. 2019. The framework for sustainable leather manufacture Second edition. United Nations. Available from: https://leatherpanel.org
2. Thorstensen T. 1993. Practical Leather Tehnology. 4rd ed. Florida, New York: Robert E. Keiger Publishing Company Malabar; 1993.

3. Crudu, M., V. Deselnicu, I. Ioannidis, L. Albu, and A. Crudu. 2012. New wet white tanning agents and technology. Proc. 4th Int. Conf. Adv. Mater Syst. ICAMS. 27–34.
4. Zuriaga-Agustí, E., M. V. Galiana-Aleixandre, A. Bes-Piá, J. A. Mendoza-Roca, V. Risueño-Puchades, and V. Segarra. 2015. Pollution reduction in an eco-friendly chrome-free tanning and evaluation of the biodegradation by composting of the tanned leather wastes. J Clean Prod. 87:874–881. Doi: 10.1016/j.jclepro.2014.10.066
5. Moussavi, G., F. Jiani, and S. Shekoohiyan. 2015. Advanced reduction of Cr(VI) in real chrome-plating wastewater using a VUV photoreactor: Batch and continuous-flow experiments. Sep. Purif. Technol. 151:218–224. Doi: 10.1016/j.seppur. 07.047
6. China, C. R., M. M. Maguta, S. S. Nyandoro, A. Hilonga, S. V. Kanth, and K. N. Njau. 2020. Alternative tanning technologies and their suitability in curbing environmental pollution from the leather industry: A comprehensive review. Chemosphere. 254:126804. Doi: 10.1016/ j.chemosphere.2020.126804
7. Kanagaraj, J., T. Senthilvelan, R. C. Panda, and S. Kavitha. 2015. Eco-friendly waste management strategies for greener environment towards sustainable development in leather industry: A comprehensive review. J. Clean Prod. 89:1–17. Doi: 10.1016/j.jclepro.2014.11.013
8. Ockerman, H. W. and L. Basu. 2014. Hides and skins. Encycl. Meat Sci. 1:112–124.
9. John, G. 1996. Possible defects in leather production. Lampertheim: Europaring 24 D-68623.
10. Covington, A. 2009. Tanning chemistry the science of leather. Northampton: Royal Society Of Chemistry.
11. Sreeram, K. J. and T. Ramasami. 2003. Sustaining tanning process through conservation, recovery and better utilization of chromium. Resour. Conserv. Recycl. 38:185–212.
12. Madhan, B., B. U. Nair, and A. Fatmawati. 2001. Tanning agent based on mixed metal complexes of Aluminium and Zinc. J. Am Leather Chem. Assoc. 343–349.
13. Bacardit, A., S. Van Der Burgh, J. Armengol, and L. Ollé. 2013. Evaluation of a new environment friendly tanning process. J. Clean Prod. 65:568–573. Doi: 10.1016/j.jclepro.2013.09.052
14. Churchill, J. 1993. Tanning skins and furs. Stackpole Books. USA.
15. Covington, A. D. and R. W. William. 2020. Tanning chemistry 2nd Edition. CPI Group (Ptd). Uk
16. Anggriyani, E., L. Rachmawati, and N. P. Adetya. 2021. The use of non-chrome mineral tanning materials as a preferable environmentally friendly tanning material. Leather Footwear J. 21:173–182.
17. Gao, D., Y. Cheng, P. Wang, F. Li, Y. Wu, and Lyu. 2020. An eco-friendly approach for leather manufacture based on P (POSS-MAA)-aluminum tanning agent combination tannage. J. Clean Prod. 257:120546. Doi: 10.1016/j.jclepro.2020.120546
18. Fuck, W. F., M. Gutterres, N. R. Marcílio, and S. Bordingnon. 2011. The influence of chromium supplied by tanning and wet finishing processes on the formation of Cr(VI) in leather. Brazilian J. Chem. Eng. 28:221–228.
19. Raghava Rao J., N. K. Chandrababu, C. Muralidharan, B. U. Nair, P. G. Rao, and T. Ramasami. 2003. Recouping the wastewater: A way forward for cleaner leather processing. J. Clean Prod. 11:591–599.
20. Krishnamoorthy, G., S. Sadulla, P. K. Sehgal, and A. B. Mandal. 2012. Green chemistry approaches to leather tanning process for making chrome-free leather by unnatural amino acids. J. Hazard Mater 215–216:173–182. Doi: 10.1016/j.jhazmat. 2012.02.046
21. Shi, J., R. Puig, J. Sang, and W. Lin. 2016. A comprehensive evaluation of physical and environmental performances for wet-white leather manufacture. J. Clean Prod. 139:1512–9. Doi: 10.1016/j.jclepro.2016.08.120