THE USE OF NON-CHROME MINERAL TANNING MATERIALS AS A PREFERABLE ENVIRONMENTALLY FRIENDLY TANNING MATERIAL

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ABSTRACT. Mineral chrome tanning agent is the most widely used tanning agent for various types of leather articles, given its various advantages. Besides its many advantages, there is a negative side to chrome tanneries, namely the presence of waste disposal that is harmful to the environment. Therefore, this study aims to determine the quality of mineral tanning materials other than chrome (aluminium and titanium) as a substitute for leather tanning (free of chrome). The research raw materials were 12 pieces of pickled goatskin. The chemicals used are aluminium tanning agent (Novaltan Al), titanium tanning agent, salt (NaCl), Peramit MLN, Derminol OCS, MgO, $NaHCO_3$, BCG indicator, Rellugan GT 50, Tanigan PAK, Lipoderm Liquor SAF, Dermagen GPA, Derminol SPE, Derminol NLM, Acid dyestuff, formic acid, Sincal DR and anti-fungal. The method used is to carry out the tanning process using aluminium tanning agents with levels of 2%, 4%, and 6% Al_2O_3, continued the combination between aluminium and titanium tanning agent. The results obtained were analyzed for the cross-sectional and content of the leather using the EDX method, a shrinkage temperature (Ts) test, and physical quality of crust skin. The results showed that the higher the Al_2O_3 content, the more Al content in the leather, but the lower the wrinkle temperature of the leather. Meanwhile, the longer the processing time, the aluminium content in the skin increases. The use of aluminium and titanium tanning agent can improve the physical quality of the skin, both in terms of tensile strength and skin softness. The conclusion that can be drawn is the use of 2% free of chrome (aluminium) tanning material can produce Ts of 71°C. The physical quality of the crust skin from aluminium and titanium mineral tanning agents is better than the single-use of aluminium.

KEY WORDS: free of chrome, mineral tanning agent, aluminium, titanium

UTILIZAREA AGENȚILOR TANANȚI MINERALI FĂRĂ CROM CA MATERIALE DE TĂBĂCIRE PRIETENOASE CU MEDIUL

REZUMAT. Agentul de tăbăcire pe bază de crom este cel mai utilizat agent tanant pentru diferite tipuri de articole din piele, având în vedere avantajele multiple ale acestuia. Pe lângă numeroasele sale avantaje, există un neajuns pentru tăbăcăriile care folosesc crom, și anume necesitatea de a elimina deșeurile nocive pentru mediu. Prin urmare, acest studiu își propune să determine calitatea materialelor de tăbăcire minerale, altele decât cromul (aluminiu și titan), ca înlocuitori pentru tăbăcirea pielii (fără crom). Materiile prime folosite în cercetare au fost 12 bucăți de piele de capră piclată. Substanțele chimice utilizate au fost: un agent de tăbăcire pe bază de aluminiu (Novaltan Al), un agent de tăbăcire pe bază de titan, sare (NaCl), Peramit MLN, Derminol OCS, MgO, $NaHCO_3$, indicator BCG, Rellugan GT 50, Tanigan PAK, Lipoderm Liquor SAF, Dermagen GPA, Derminol SPE, Derminol NLM, colorant acid, acid formic, Sincal DR și agent antifungic. Metoda utilizată este realizarea procesului de tăbăcire folosind agenți pe bază de aluminiu cu conținut de Al_2O_3 în proporții de 2%, 4% și 6%, continuându-se cu o tăbăcire combinată cu agenți pe bază de aluminiu și titan. S-au analizat pieile obținute pentru a determina conținutul de aluminiu în secțiune transversală folosind metoda EDX, temperatura de contracție (Ts) și calitatea fizică a pielii crust. Rezultatele au arătat că, cu cât este mai mare conținutul de Al_2O_3, cu atât este mai mare conținutul de Al în piele, dar cu atât este mai scăzută temperatura de contracție. Pe de altă parte, cu cât timpul de prelucrare este mai mare, conținutul de aluminiu din piele crește. Utilizarea agentului de tăbăcire din aluminiu și titan poate îmbunătăți calitatea fizică a pielii, atât în ceea ce privește rezistența la tracțiune, cât și moliciunea pielii. Concluzia care poate fi trasă este că utilizarea agenților tananți fără crom (aluminiu) în proporție de 2% poate conduce la obținerea Ts de 71°C. Calitatea fizică a pielii crust tăbăcită combinat cu agenți pe bază de aluminiu și titan este mai bună decât în cazul utilizării simple a aluminiului.

CUVINTE CHEIE: fără crom, agent de tăbăcire mineral, aluminiu, titan

L'UTILISATION DES AGENTS DE TANNAGE MINÉRAUX SANS CHROME COMME MATÉRIAUX DE TANNAGE RESPECTUEUX DE L'ENVIRONNEMENT

RÉSUMÉ. L'agent tannant au chrome est l'agent tannant le plus utilisé pour divers types de maroquinerie, compte tenu de ses nombreux avantages. Outre ses nombreux avantages, les tanneries qui utilisent du chrome présentent un inconvénient, à savoir la nécessité d'éliminer les déchets nocifs pour l'environnement. Par conséquent, cette étude vise à déterminer la qualité des matériaux de tannage minéraux, autres que le chrome (aluminium et titane), en tant que substituts pour le tannage du cuir (sans chrome). Les matières premières utilisées dans la recherche étaient 12 pièces de peau de chèvre piclée. Les produits chimiques utilisés étaient : un agent tannant à base d'aluminium (Novaltan Al), un agent tannant à base de titane, sel (NaCl), Peramite MLN, Derminol OCS, MgO, $NaHCO_3$, indicateur BCG, Rellugan GT 50, Tanigan PAK, Lipoderm Liquor SAF, Dermagen GPA, Derminol SPE, Derminol NLM, colorant acide, acide formique, Sincal DR et agent antifongique. La méthode utilisée consiste à réaliser le procédé de tannage à l'aide d'agents à base d'aluminium contenant de l'Al_2O_3 dans des proportions de 2%, 4% et 6%, en poursuivant par un tannage combiné avec des agents à base d'aluminium et de titane. Les cuirs obtenus ont été analysés pour déterminer la teneur en aluminium en section transversale par la méthode EDX, la température de retrait (Ts) et la qualité physique du cuir en croûte. Les résultats ont montré que plus la teneur en Al_2O_3 est élevée, plus la teneur en Al dans la peau est élevée, mais plus la température de retrait est basse. D'autre part, plus le temps de traitement est long, plus la teneur en aluminium du cuir est élevée. L'utilisation d'agent tannant à l'aluminium et au titane peut améliorer la qualité physique de la peau, tant en termes de résistance à la traction que de douceur de la peau. La conclusion que l'on peut en tirer est que l'utilisation d'agents tannants sans chrome (aluminium) dans la proportion

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de 2% peut conduire à une Ts de 71°C. La qualité physique du cuir en croûte tanné aux agents à base d'aluminium et de titane est meilleure qu'avec la simple utilisation de l'aluminium.
MOTS CLÉS : sans chrome, agent tannant minéral, aluminium, titane

INTRODUCTION

Leather tanning is an industry that needs special attention given to the many challenges it faces. The thing that needs to be seen further is about environmental sustainability for the next life of mankind. Without paying attention to environmental sustainability, the production processes of various industries will only focus on profit alone.

Environmental sustainability can be achieved if every aspect of life is considered without damaging the environment. Tanning is an industry that faces the perception that it contributes to environmental damage, namely the large waste produced and the irreversible raw materials used. Therefore, it is important to try to replace tanning materials with materials that are more environmentally friendly. Furthermore, the materials used so far are mostly hazardous to health or carcinogenic substances. If this material is used continuously for a long period of time it can endanger the health of tanners as well as those who use leather products.

The tanning materials that have been used include chrome, vegetable, aldehyde, and others. There should be an effort to try other tanning materials that are still acceptable to consumers and still have good quality (according to standards). Chromium is one of the most important environmental problems related to leather tanning. The most commonly used leather tanning process is chrome tanning. This implies the presence of chromium in both liquid waste and leather waste. Leather waste must be disposed of in landfills which causes a large environmental impact and high costs [1]. The negative impact of this chrome tanning agent is when Cr (III) changes to Cr (VI). Although there is a solution to reduce Cr (VI), that is, adding a vegetable tanning agent which can reduce the formation of Cr (VI) [2]. However, solutions and studies of other mineral substances in leather tanning are still needed.

Other minerals that can be used for tanning are aluminium and titanium. Aluminium is a mineral tanning material that can be used and developed further as a tanning material that is more environmentally friendly than chrome. Aluminium as a tanning material has a Ts value of 65°C. The function of this tanning is influenced by the ligand which is combined with the metal tanning material. Aluminium tanning agent has good results but not the aluminium tanning agent by itself. Therefore, it is necessary to further study the use of aluminium as a substitute for chrome tanning. Aluminium and titanium produce white leather.

The other material example which can produce white leather is formalin. However, formalin is a toxic material that is harmful to the environment and health. Formalin can be used as a tanning agent because it contains formaldehyde. Formaldehyde is one of the simple aldehyde tanning agents [3].

The aluminium-silica tanning process produces white leather with standards that meet the automotive upholstery industry. The strong white and cationic properties make it easy to create vibrant colors. Leather processed in this way is free from chromium, aldehydes, and organic solvents [4]. Wet white skin is somewhat less stable than wet blue skin on UVA rays, because of the tendency to break the polypeptide bonds in existing cases [5].

Wet white tanning with basic ingredients from vegetable tanning agents and Laponite nanoclay produces leather with physical quality that meets standards for furniture leather, with no harmful ingredients, Cr (VI), and free from detectable formaldehyde. This system can reduce the global warming potential and human toxicity potential compared to conventional tanning processes, without using a chrome tanning agent [6].

The effect of the presence of aluminium (III) in chromium tanning has been shown to increase the rate of chromium fixation, with an effect analogous to catalysis. It can be seen that pretreatment with aluminium has a positive effect on chrome content. The reaction between carboxyl collagen and aluminium (III) is fast [7].

Aluminium salt has the advantage of being abundant and cheap. However aluminium is only loosely bound to collagen, so the reaction is opposite when the skin is wetted and in an acidic environment, for this reason, this process is considered pseudo tanning and is called pseudo tanning rather than tanning [8].

Basic aquo ions can interact electrostatically via water ligands or form complexes, which are more electrovalent than covalent. Because it is known that aluminium (III) does not form a stable complex. Therefore, the bonds between the collagen and the matrix can be broken down hydrothermally, but the aluminium core environment will not change much. Therefore, it can be concluded that the aluminium-based matrix involves water that can be broken down, which allows shrinkage, i.e. the electrostatic interaction with the carboxyl collagen is far enough away to allow this to occur, but the aluminium (III) core does not change its magnetic field. In contrast, covalent skin between carboxyl collagen and chromium (III) is a direct interaction, which cannot be broken down under shrinkage conditions. Therefore, the shrink transition cannot involve breaking metal collagen bonds, so the process must involve breaking hydrogen bonds in helix three, causing them to break down, and in the linked matrix around helix three [7]. The suspended solid content in aluminium tanning wastewater is lower than conventional chrome tanning wastewater and combined tanning wastewater. This may be due to the different amounts of tanning materials, resulting in the immobilization of large amounts of collagen in the tanning material, the remaining tanning material cannot penetrate the collagen fibers, so there is more suspended solids content [9].

Aluminium can be used as a pre-tanning material. If it is used as a pre-tanning material, it can be continued with tanning using 30% mimosa vegetable tanning, which can produce a temperature of 94.54°C [10]. Besides the increasing use of Al_2O_3, the higher the level of shrinkage temperature. However, the higher the Al_2O_3, the more it causes grain coarseness [11]. On the other hand, titanium (IV) salts have a similar affinity for collagen as aluminium (III), in part due to some similarities in properties, such as the acidity of the ion and the tendency to hydrolyze and to precipitate as the pH is raised above 3. The interaction with collagen carboxyls is similarly electrovalent, rather than covalent. However, one difference is the greater filling effect of Ti (IV) salts, due to the polymeric nature of the salts, which produces softer leather. The weak chemical interaction with collagen results in shrinkage temperatures of 75-80°C [7].

EXPERIMENTAL

Materials and Methods

Instruments

Drum trial, bucket, baumemeter, knife, thickness gauge, measuring frame, set-out knife, and tilt table.

Materials

12 pieces of pickled goatskins, with an area of 7 sq ft, thickness 0.7 - 0.75 mm.

The chemicals used are aluminium tanning agent (Novaltan Al), titanium tanning agent, salt (NaCl), Peramit MLN, Derminol OCS, MgO, $NaHCO_3$, BCG indicator, Rellugan GT 50, Tanigan PAK, Lipoderm Liquor SAF, Dermagen GPA, Derminol SPE, Derminol NLM, Acid dyestuff, formic acid, Sincal DR and anti-fungal.

Technology Process

The research was conducted by carrying out a tanning process using aluminium and titanium tanning as a substitute for chrome tanning agent. The tanning process was carried out with 3 kinds of Al_2O_3 content, namely, 2%, 4%, and 6%, and also the use of aluminium mixed with titanium (2:1).

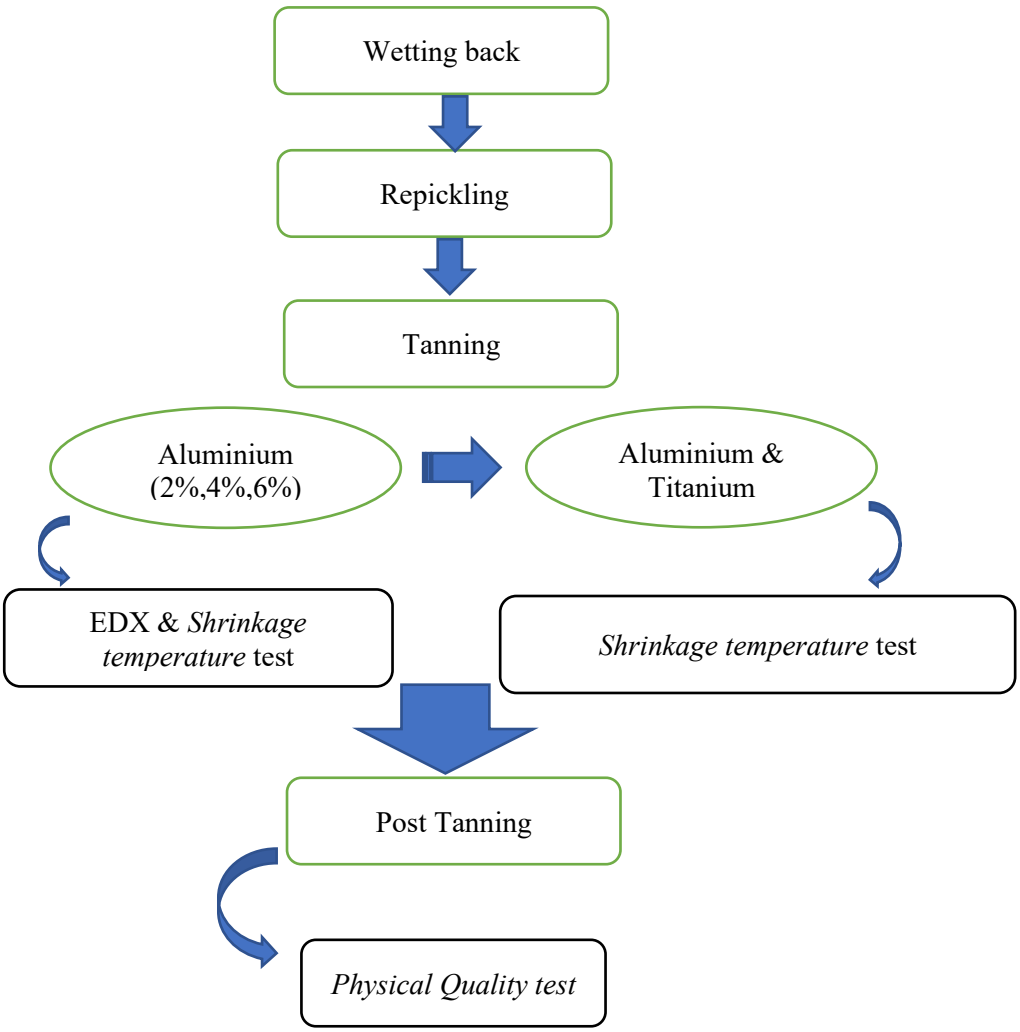


Figure 1. Research flow chart

Data Analysis

Shrinkage temperature test (Ts)

Shrinkage temperature test is a test to determine the temperature when the skin first wrinkles/shrinks. The test is carried out by cutting a skin sample and placing it in heated water. Furthermore, it is observed at what temperature the skin starts to wrinkle. The results of Ts of each treatment obtained were compared with the one-way ANOVA test. The best results of Ts then mix with titanium tanning agent.

Analysis of the Content of the Tanning Agent in the Skin

The content of aluminium tanning agent in wet white leather was then tested using the EDX (Energy-Dispersive Xray Spectroscopy) test (based on differences in concentration variations, followed by a function of time).

Physical Quality Test

The resulting crust skin was tested for tensile strength, and a test for softness using a softness meter.

RESULTS AND DISCUSSIONS

The global rise in pollution is increasingly demanding for the development of producing good quality leather that is friendly to the environment. One of the things that can be used is the use of chrome-free tanning materials. The mineral tanning material class that can be studied in more depth as a

substitute for chrome are aluminium and titanium.

Effect of Aluminium Concentration on Aluminium Levels in the Skin

Of the total amount of aluminium used in the tanning stage, some of the aluminium tanning agents will react with skin collagen and part will be carried away to the waste. After basification of aluminium compounds at the end of the tanning process with magnesium oxide, a reaction occurs between the aluminium complex and the collagen protein in which the aluminium binds directly to the carboxylate groups of collagen [12], as shown in Figure 2 and Figure 3.

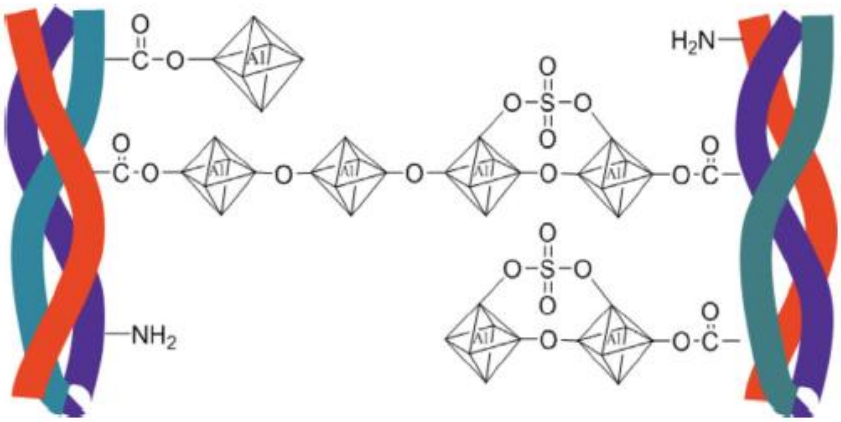


Figure 2. Representative of the bonding of aluminium tanning agents with skin collagen [13]

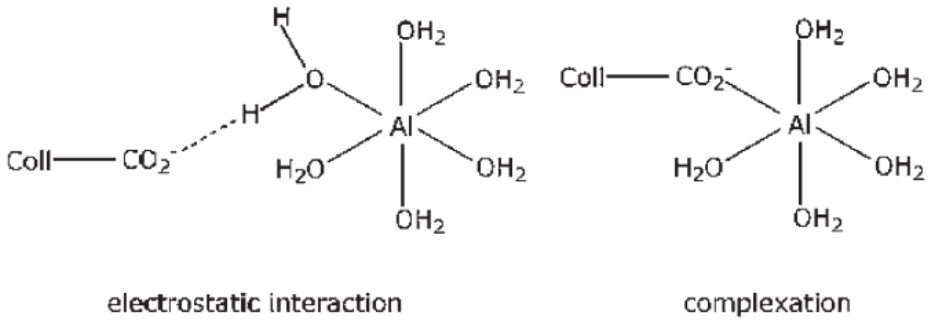


Figure 3. Interaction of Al and collagen [7]

Table 1: EDX skin results with varying concentrations of aluminium

Element	Al 2% (mass %)	Al 4% (mass %)	Al 6% (mass %)
C	43.17	48.86	45.02
N	11.07	15.06	17.35
O	34.50	25.37	32.03
Na	1.29	4.19	1.40
Mg	0.16	0.19	0.27
S	3.34	0.27	0.30
Cl	2.50	5.14	1.98
Ca	3.18	-	-
Cr	-	-	-
Al	0.79	0.93	1.64

The EDX data in Table 1 presents that the main constituent elements of the skin, whether tanned with chrome or aluminium tanning materials, are carbon, nitrogen, and oxygen which are elements commonly found in living things and are the main constituent elements of amino acids and lipids. Meanwhile, other elements, namely sodium (Na), magnesium (Mg), sulfur (S), calcium (Ca), and chloride (Cl) were also detected to be the constituent of the

skin. These elements are naturally present in the skin as mineral salts, but can also come from chemicals used in the leather tanning process such as pickling, unhairing, liming, basification, and others.

Based on Table 1, it is also seen that the aluminium content in leather at a concentration of Al_2O_3 is 2%, 4%, and 6%. The higher the number of Al_2O_3 used, the higher the aluminium content in the skin. This shows that the aluminium used is still acceptable on the skin with the increasing amount of Al_2O_3 used. The more aluminium content in the skin it is expected that the more aluminium will be bound to the carboxylate group of the skin, so that the tanning will be better.

Cross-section of Wet White Skin

Figure 4 is a picture of goatskin before and after the wet white tanning process is carried out. It can be seen in the picture that the result of aluminium tanning and mixed aluminium and titanium is skin that is evenly white or so-called wet white, which is different from the skin from chrome tanning agent which produces wet blue skin.

a. Pickled skin

b. Wet white aluminium

c. Wet white aluminium & titanium

Figure 4. Goatskins

Effect of Tanning Time on Aluminium Levels in the Skin

Table 2 describes that the longer the processing time, the higher the aluminium content in the skin. This shows that the processing time is important to achieve the target of penetration of the tanning material into the skin. The process of tanning and complex formation is not an instant reaction. The rate of reaction changes with pH conditions and process temperature [7]. Good control of the quality of the tannery requires adherence to the established temperature, pH, and time relationships.

Table 2: The level of aluminium in the skin based on the processing time

*Tanning time (hour)	Aluminium in the skin (%)
1	0.53
4	1.00
7	1.09
10	1.04

*concentration Al = 2 %

The shrinkage temperature of wet white TVT increased with the length of tanning time and remained stable after 3 hours of tanning [14]. Therefore, the optimal tanning duration is set to be 4-5 hours. This shows the importance of processing time to reach mature skin and a certain wrinkle temperature.

Shrinkage Temperature (Ts) of Wet White Tanning Agent

Table 3: Results of mean pH and shrinkage temperature (Ts)

Tanning agent	%	Pickled skin		Wet white	
		pH	Ts (°C)	pH	Ts (°C)
Aluminium	2	2.5	42	3.9	71
	4	2.5	43	3.9	69
	6	2.5	43	3.8	68
Aluminium : Titanium	2 : 1	2.5	43	4.5	73

Based on Table 3, it can be seen that the shrinkage temperature of wet white is lower than that of wet blue because chrome tanned leather still has the highest Ts value (±100°C). Even the shrinkage temperature between exhausted and conventional tanning chrome has different results. The shrinkage temperature for skin with an exhausted tanning system has higher heat resistance than others [15]. There is a difference in the temperature of the pickled skin wrinkle with the wet white aluminium skin. After the skin was tanned, there was an increase in the temperature of the wrinkle (shrinkage temperature). Pickled skin has an initial pH of 2.5 then after aluminium tanning, the pH is 3.8 - 3.9. The increase in pH is in line with the increase in the wrinkle temperature of the skin from pickled skin to wet white skin. According to Li [14], it is clear that the wrinkle temperature of wet white increases with increasing pH. When the pH of the tanning is higher, a shrinkage temperature of around 90°C is reached, which indicates strong tanning ability. The number of carboxylate groups on the collagen side chain increases with increasing pH, which supports the equalization of the carboxylate groups with aluminium.

Goatskin that is tanned with aluminium tanning material can produce wet white leather with a shrinkage temperature of ± 70°C. This Ts is lower than chrome tanning which is capable of up to 100 or 120°C. However, the maximum performance of a tannery Ts is not a benchmark, the benchmark is what the final result of the leather product will be made of, requiring high heat resistance. So that with the performance of Ts 71°C, 69°C, 68°C, and also 73°C from a mix of aluminium and titanium, it is still acceptable or it is said that the skin is tanned ripe. The combination tanning agent between aluminium and titanium can reach higher Ts. Based on the results of shrinkage temperature testing, it can be seen that the higher the Al_2O_3 content used for tanning, the lower the Ts achieved. Based on these results, it can be said that although the aluminium content in the skin increases with the addition of Al_2O_3 used (Table 1), it does not mean that the higher the aluminium binds to the carboxylate. There is an indication that the aluminium in the skin is only penetrated and has not been bonded. This is following that if the tanning material is too excessive, it is feared that there will be aluminium in the collagen structure but it is not chemically bound to the collagen protein carboxylate group (appears as dissolved aluminium in the skin) [12]. So as a result, if the aluminium does not bind to the skin, the Ts obtained will be low.

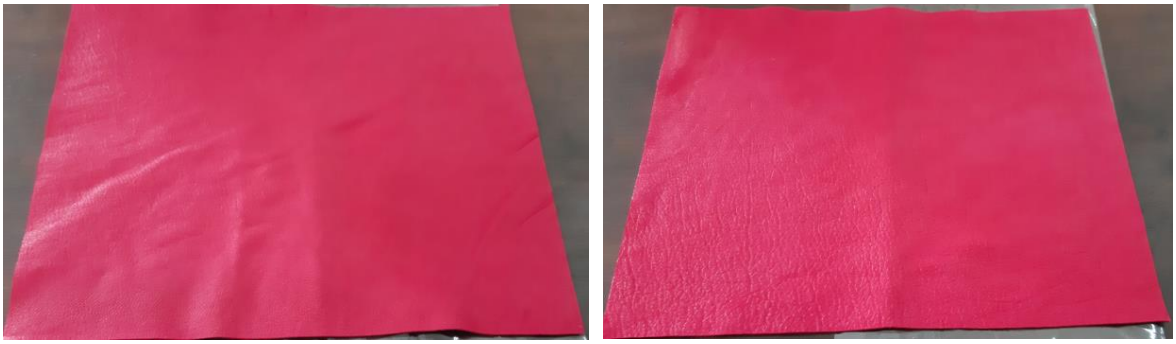
Table 4: ANOVA Ts test results on the three variations of Al_2O_3

Variable	Content of Al_2O_3			*P* value
	2%	4%	6%	
Ts (°C)	70.67 ± 0.58	69 ± 1	67.67± 10.58	0.008

The value of the shrinkage temperature changes with alterations in the amount of tanning material used. Based on the results in Table 4, it shows these changes, then when tested by ANOVA (Table 4) it can be seen that the results of Ts (shrinkage temperature) at the variation of 2%, 4%, and 6% have a significant difference ($p < 0.05$). This indicates that the use of tanning agents affects the yield of Ts obtained from aluminium tanning agents.

Although the results obtained are inversely proportional. If there is no bonding with the collagen carboxylate group, the wrinkle temperature (Ts) will be low. This indicates that the increase in the amount of tanning material used for tanning does not result in an increasing number of wrinkles. The use of a 2% aluminium tanning agent is capable of tanning the skin with an average performance of Ts 71°C.

After analyzing the quality of the tanning leather, then the leather with the percentage of 2% Al_2O_3 and the mix between aluminium and titanium was carried out post tanning process to produce crust dyed leather. The part of the crust dyed skin that has been cut is shown in Figure 5.



a. Aluminium b. Aluminium & Titanium

Figure 5. Crust dyed skin

Based on Figure 5, it can be seen that leather tanned using aluminium and titanium has good color evenness. This shows that this mineral tanning material also has good color quality results when used for colored leather products. The results of the physical quality of the crust, both tensile strength and flexural strength, are shown in Table 5.

Table 5: Physical quality of crust dyed skin

Tensile strength (N/mm)		Softness (mm)	
Aluminium	Aluminium & Titanium	Aluminium	Aluminium & Titanium
17.61	25.05	3.9	4.5
16.59	50.91	3.5	3.75
13.15	50.88	3.4	3.3

Based on Table 5, it can be seen that the leather produced from mineral tanning materials other than chrome can produce physical qualities that can be compared with certain articles. The use of aluminium and titanium tanning materials simultaneously in the tanning process can improve the physical quality of the skin, both in terms of tensile strength and skin softness. This can be used as a consideration for the use of other mineral tanning materials other than chrome to produce leather. The use of titanium (IV) tanning material has advantages such as having a shrinkage temperature of Ts = 76.1°C and chromium-free waste production. In addition, it can also improve the quality of non-allergenic products because titanium (IV) salt is harmless and does not cause problems for sensitive skin or mucous membranes [16].

CONCLUSIONS

Aluminium and titanium tanning agents are proven to be able to be used for tanning skin, by penetration of the tanning agent into the skin and achieving the desired wrinkle temperature. The higher the Al_2O_3 used, the higher the aluminium content in the skin. The higher the Al_2O_3 used, the lower the shrinkage temperature (Ts) obtained, this is related to the bond between the tanning material and skin collagen, not only penetrated in the skin.

The use of Al_2O_3 2% can be used for tanning with a shrinkage temperature (Ts) of 71°C. The physical quality of the crust skin from mixed aluminium and titanium mineral tanning agents is better than the single-use of aluminium, as a driving force for chrome-free tanning agents.

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