GSC Advanced Research and Reviews
eISSN: 2582-4597 CODEN (USA): GARRC2
Cross Ref DOI: 10.30574/gscarr
Journal homepage: https://gsconlinepress.com/journals/gscarr/

(Research Article)

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Assessment of ultrasonic influence on titanium tanning leather stability

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GSC Advanced Research and Reviews, 2023, 15(02), 001–007

Publication history: Received on 07 March 2023; revised on 13 April 2023; accepted on 16 April 2023

Article DOI: https://doi.org/10.30574/gscarr.2023.15.2.0122

Abstract

Ultrasound effects on titanium tanning of leather were studied. 30 kHz and 60 kHz ultrasound were applied to cattle skins during titanium tanning. The study included five different treatment conditions, examining effects such as leather shrinkage temperature (Ts), titanium content, and distribution. Heat loading was controlled. Results indicated that 30 kHz ultrasound improved titanium agent penetration and increased shrinkage temperature, while 60 kHz produced minimal improvements. A maximum shrinkage temperature of 107.9 °C was achieved using 30 kHz ultrasound pretreatment of tanning liquor, followed by 30 kHz ultrasound in the tanning mixture in a salt-free medium. Ultrasound was found to enhance titanium tanning and create superior mineral-tanned leather.

Keywords: Titanium agent; Ultrasonic influence; Tanning; Leather stability

1. Introduction

Chromium is an excellent tanning agent for leather, but there are three major issues associated with its use that make it difficult to continue relying on it. Firstly, chromium is a finite resource, which means its availability is limited. Secondly, its safety record is concerning and needs to be approached with caution. Finally, uncontrolled emission of chromium during tanning can cause significant harm to the environment [1]. An ideal replacement for chromium as a tanning agent should be abundant, affordable, environmentally friendly, and provide comparable performance for tanned leather. Additionally, it should be user-friendly and safe. [2]. Titanium is a readily available metal salt with strong tanning capabilities that makes it a promising alternative to other tanning agents. It is abundant in nature, non-toxic, and offers superior performance in comparison to other metal tanning agents when used to tan leather [3]. So, Titanium tanning has emerged as a highly viable alternative to chromium tanning in the modern leather industry. In recent times, significant strides have been made in enhancing the efficacy of titanium tanning. [4]. A new tanning agent based on Ti (IV) sulfate has shown superior tanning capabilities compared to traditional titanium tanning agents. However, its effectiveness is hindered in conventional tanning processes due to the inability of Ti (VI) complex molecules to penetrate the hide. This is due to the broad size range of the titanium coordination compounds, which can exist as large molecules, titanium colloids, or particulate aggregates with very large particle sizes, particularly at higher pH levels in titanium liquors [4]. To achieve complete and effective tanning agent penetration and enable full reaction and complexation with the hide's collagen matrix, it is essential to explore alternative methods to traditional drumming. Power ultrasound refers to a specific range of sound waves, typically between 20 kHz to 100 kHz, although it can extend from 18 kHz to 1 MHz. Its unique ability to enhance various chemical reactions and processes, including leather processing, has been attributed to a phenomenon known as cavitation. This involves the growth and collapse of microscopic bubbles resulting from compression and rarefaction cycles when sound waves pass through a liquid medium. These cavitations lead to significant mechanical and chemical effects such as agitation, dispersion, emulsification, degreasing, micro-jetting, and free radical production. [6]. Research on the applications of ultrasound in leather processing has been ongoing for over 50 years, with promising results. Ultrasound has been found to enhance numerous steps in the leather processing chain, including soaking, degreasing, unhairing, liming, fatliquoring, dyeing,

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and wastewater treatment. [6–12]. Ultrasound has matured into a technology that effectively improves the efficiency of various manufacturing processes, including the production of different materials. It presents a promising opportunity for minimizing the number and types of chemicals utilized in leather production. In an effort to enhance the penetration of titanium complexes into hides and increase the tanning effect of titanium agents, power ultrasound was utilized in titanium tanning. The process was conducted using an ultrasonic tanning apparatus, as well as a distinct ultrasonic drum that combines the mechanical action of rotational mixing and elastic compression/extension of hides with ultrasonic irradiation. Ultrasonic parameters such as frequency, power, and duration can have a significant impact on the tanning process [6, 7]. In this study, power ultrasound was used during titanium tanning under various conditions, including different dosages and alkalinities of the tanning agent, two frequencies of ultrasound (30 and 60 kHz) during tanning, three different tanning mediums, and an ultrasound-pretreated tanning agent. The study evaluated the ultrasonic effect on titanium tanning through various treatments, including assessing titanium content, distribution, and the leather's shrinkage temperature.

2. Material and methods

2.1. Preparation of Titanium tanning solution

A molar ratio of 0.8: 1.2 was used as titanium tanning agents in this investigation [4]. The titanium oxide content was 90 g/l and the alkalinity was adopted to 40% or 60% with solution of Na_2CO_3.

2.2. Cattle skin preparation

Cattle skins were pickled using the traditional leather-making process. Next, they were neutralized to pH 7.0 with sodium bicarbonate in an 8% salt solution to create depickled skin. Afterward, the depickled cattle skins were washed thoroughly to eliminate salts. Finally, the skins were cut into approximately 20 g pieces and used in our experimental design, with chemical dosages based on the weight of the 75% moisture depickled pigskin.

2.3. Ultrasonic tanning apparatus

Two methods were used for ultrasonic titanium tanning, utilizing an ultrasonic tanning apparatus and a distinctive ultrasonic drum. The former utilized a CBS-1 ultrasound generator with a variable power output range of 80-230 W and a probe-type transducer. The tanning vessel was a columned glass container with a diameter of 6.5 cm and was immersed in a temperature-controlled water bath/shaker that provided both shaking action and oscillator vibrations to the samples.

The lab-scale ultrasonic drum comprised of six plate-type ultrasound transducers and an ultrasound generator with a 1.5 kW power output. The tanning vessel, a specially designed drum with wire mesh walls and face, was submerged in the tanning liquor and rotated automatically, allowing the liquid to freely enter and exit through the openings. The drum had a diameter of 300 mm and a total tanning bath volume of 1500 ml. The ultrasound had a fixed frequency of 28.4 kHz, and the ultrasound power density was 227.1 W/cm2 in experiments, calculated as the electric power divided by the transducer's surface area [5].

2.4. Titanium tanning methods

2.4.1. Titanium tanning in the ultrasonic tanning apparatus

For comparison between titanium tanning with and without ultrasound, paired skin pieces with an average mass of 20 g were cut from the same depickled skin. The experiment involved placing two skin pieces into the tanning vessel with 120 ml of one of three different fluids: H_2O, 6% (w/w) NaCl solution, or 1% (w/w) Picaltal Flakes solution (a non-salt pickling agent from BASF Company). All other conditions were held constant.

The vessel was stirred at 25 ^oC for 30 min, and then titanium tanning liquors with varying basicity (40% or 60%) and dosages (5% or 10% amount based on TiO_2) were added to the vessel, with or without ultrasound pretreatment. Once titanium had penetrated the skin's inner portions, the tanning bath was gradually basified to pH 3.7 using 100 g/L $NaHCO_3$ solution, within a maximum of 4 h. The temperature of the tanning bath was then increased to 40 ^oC, and the vessel was continuously stirred for another 2 h at 40 ^oC. Tanning was conducted under continuous mechanical stirring (50 rpm), with or without ultrasound irradiation.

Power ultrasound (30 kHz or 60 kHz frequency) was applied to the tanning process continuously for up to 12 h in 80 min cycles (60 min ON and 20 min OFF), from the introduction of the tanning agent until completion. Ti uptake was determined by analyzing a small aliquot of tanning solution taken at regular time intervals, and was calculated based on the weight of the depickled skin with 75% moisture content. Shrinkage temperature of a small piece of tanned leather was measured regularly. After aging for 48 h, the leathers were split into three layers and the TiO_2 content of each layer was analyzed.

2.4.2. Titanium tanning in the ultrasonic drum

Half Cattle skins pieces were tanned in the ultrasonic drum with or without ultrasound as per the following (Table 1) recipe

Table 1 Recipe of titanium tanning in Ultrasonic Drum

Parameters	**Conditions**
Water	300 at 25°C
Picaltal Flakes solution	1.5% for 60 minutes
fatliqour	1% for 30 minutes
Titanium tanning liquids	5% for 180 minutes
Magnesium oxide	0.5% 120 minutes
Hot water	100% 60 minutes
pH	Checked overnight 4.0

Ultrasound was used in 80-minute cycles during the tanning process, with 60 minutes of application followed by 20 minutes of rest. A control group of half piece skin was tanned under identical conditions, but without ultrasound. Both sets of tanned leather underwent conventional post-tanning procedures such as neutralization, dyeing, fatliquoring, drying, and softening. Finally, the organoleptic properties of the leathers, including softness, fullness, firmness, appearance, etc., were assessed.

2.5. Procedure of Analysis

The leather shrinkage temperature meter was used to measure Thermal Shrinkage temperature, with water used as the fluid for temperatures below 95°C and a 75:25 glycerol-water solution for temperatures above 95°C. Titanium content was determined using UV absorption spectrophotometry, with spent titanium tanning liquors and titanium-tanned leather samples digested using nitric and sulfuric acid. The resulting clear digest solutions were diluted and reacted with hydrogen peroxide, producing a yellow solution with absorbance measured at 407 nm using a Shimadzu UV2501PC spectrophotometer. To determine the titanium concentration (expressed as TiO_2), appropriate standards were used to create a calibration curve for comparison. Ti uptake and Ti-absorbed ratio were calculated as follows: Ti uptake = (Ci - Ct) X V/W, where Ci and Ct represent the titanium concentration of the tanning bath at the start and time t, respectively, V is the total volume of the tanning bath, and W is the weight of the skin (with 75% moisture content). Ti-absorbed ratio = (Ci -Ce)/Ci X 100%, where Ci and Ce represent the titanium concentration of the tanning bath at the start and end of tanning, respectively.

3. Results and discussion

Tanning is a chemical process that introduces additional crosslinks into collagen, binding tanning agents to protein functional groups. The extent of cross-linking between collagen molecules and the thermodynamic stability of the cross-linking bonds determines the tanning effect. The shrinkage temperature, which indicates the start of leather formation, is a crucial parameter. Penetration of tanning agents is also significant for characterizing the tanning process, given the substantial thickness of animal skins or hides. Good penetration and uniform distribution of tanning materials across the hide cross-section are essential for achieving a satisfactory tanning effect. Tanning agent uptake, titanium distribution in the leather, and shrinkage temperature were used to assess tanning effects in this study. However, animal hides are non-uniform, with significant variations in thickness and fibril weaving types in different areas. To address this, skin pieces from adjacent positions were selected in each sampling group, with one serving as the control for each experiment. Within-experiment results are comparable, but between-experiment results may not be comparable due to inhomogeneities in sampling. Tanning is a two-step process involving tanning agent penetration followed by pH-dependent fixation [9].

3.1. Effects of ultrasound on titanium uptake

Tanning effectiveness is determined by tanning agent penetration and distribution in the leather, which are critical factors influencing the tanning effects and ultimate properties of the leather. Therefore, the standard tanning practice involves penetration followed by fixation. In metal (mineral) tanning, penetration occurs at a low pH since the metal ions cannot complex easily with collagen and mainly penetrate the hides.

Metal tanning involves raising the pH through basification to allow for the combination of the tanning material with collagen in the skins. Although some tanning agent binds during penetration, more titanium combines with skin proteins during basification (pH increases from approximately 1.2 to 3.7). Table 1 summarizes the Titanium (Ti) uptake with and without power ultrasound after basification.

With and without ultrasound, Titanium (Ti) uptake for the 5% offer is 48.90 and 40.80 mg TiO_2/g skin, respectively, while for the 10% offer the Titanium (Ti) uptake is 65.60 and 55.45 mg TiO_2/g skin, respectively. Ultrasonic treatment results in a 19.95% increase (8.1 mg TiO_2/g skin) in Titanium (Ti) uptake for the 5% offer and a 18.30 % increase (10.15 mg TiO_2/g skin) for the 10% offer [5].

Ultrasound enhances Titanium (Ti) uptake and Titanium (Ti) absorbed ratio during basifying stage of tanning (Table 2). For 5% offer, Titanium (Ti) uptake is 48.90 and 40.80 mg TiO_2/g skin with and without ultrasound, respectively, while Titanium (Ti) absorbed ratio is 85.30% and 70.23% with and without ultrasound, respectively. For the 10% offer, Titanium (Ti) uptake is 65.60 and 55.45 mg TiO_2/g skin with and without ultrasound, respectively, and Titanium (Ti) absorbed ratio is 65.43% and 56.20% with and without ultrasound, respectively. The ultrasonic effect is 8.1 mg TiO_2/g skin (19.95% increase) for 5% offer and 10.15 mg TiO_2/g skin (18.30% increase) for 10% offer. As the ultrasonic effect is greater for the lower offer, 5% TiO_2 offer was used in the following tanning experiments [11].

Table 2 Titanium uptake after Alkalinity

offer	Titanium Oxide up take		Titanium absorbed Ratio	
	With ultrasound	**Without ultrasound**	**With ultrasound**	**Without ultrasound**
5%	48.90	40.80	85.30	70.23
10%	65.60	55.45	65.43	56.20

Table 3 shows a comparison of tanning with and without ultrasound at 30 kHz. With power ultrasound, titanium content, uniformity, and shrinkage temperature all show clear superiority. Compared to without ultrasound, the titanium uptake and uniformity are roughly 4% and 12% better, respectively, while the shrinkage temperatures are similar.

Table 3 Comparison of tanning effects with and without ultrasound

Parameters	With ultrasound	Without ultrasound
Titanium oxide (TiO_2) in leather	18.46	16.36
Uniformity of titanium distribution, %	85.45	75.23
Shrinkage temperature Ts, ^oC		
Grain layer	96.6	94.5
Middle layer	90.5	88.7
Flesh layer	98.4	95.3

3.2. Factors influencing effectiveness of ultrasonic titanium tanning

3.2.1. Tanning medium

Metal tanning is typically done in a highly concentrated pickling solution with more than 6% NaCl to prevent acidic swelling of the hide that can weaken leather strength [13]. Conventional titanium tanning also uses a pickling solution. Previous research [4] has shown that titanium tanning agents can better penetrate the skin when tanning in a NaCl solution compared to water. However, NaCl can also decrease the affinity and reactivity of the titanium tanning agent with collagen. The high affinity of titanium with collagen in a water medium makes it more challenging for titanium to penetrate into the hide. Titanium tanning in a high-salt pickling solution reduces its effectiveness, as the cross-linking between collagens and Ti-complexes becomes more challenging. Thin skins, such as goatskin under 2.5mm thickness, can achieve high tanning strength (Ts) in water-based titanium tanning [4]. However, skins thicker than 4.0mm can experience acid swelling in the middle layer, hindering the penetration of Ti-complexes. Therefore, thick hides require a non-swelling pickling agent instead of NaCl, while thin skins can be directly tanned in water.

Table 4 shows that the combination of 1.0% Picaltal Flakes and ultrasound produces the highest titanium content, uniformity, and shrinkage temperature. The treatment with 6% NaCl medium and no ultrasound has the lowest titanium content and shrinkage temperature with mediocre penetration. The performances of the 1.0% Picaltal Flakes solution and water treatments are similar, with the leather tanned in Picaltal Flakes having higher shrinkage temperature due to more uniform titanium distribution. Notably, cattle skin tanned with 1.0% Picaltal Flakes and 20 kHz ultrasound achieves a very high shrinkage temperature of 107.9 °C, a record to our knowledge. Comparing the last two columns in Table 4, ultrasound increases titanium content by 2.8%, uniformity by 20.1%, and enhances shrinkage temperature by 5.3%, indicating substantial overall improvements [13].

Table 4 Influence of tanning medium on effectiveness of 30 kHz ultrasonic tanning

Offer	**Without ultrasound**			**With ultrasound**
	Water	6% NaCl	1% Picaltal Flakes	1% Picaltal Flakes
Titanium oxide (TiO_2) in leather	20.45	19.35	20.96	21.55
Uniformity of titanium distribution, %	55.64	73.44	65.20	78.30
Shrinkage temperature, Ts, °C after basification	98.5	95.5	102.5	107.9

3.2.2. Alkalinity of titanium tanning liquor

Alkalinity is a crucial property of mineral tanning agents that reflects both molecular size and reactivity. Higher basicity indicates a larger molecular size and greater reactivity. In this experiment, tanning was done in a water-only medium, and titanium tanning was performed with 40% or 60% basicity of the tanning agent at 5% offer level with or without 30 kHz ultrasound. Table 5 compares titanium content, uniformity, and shrinkage temperature for two levels of basicity with and without ultrasound. The best tanning effectiveness was achieved with 40% basicity and ultrasound, and the worst performance came from 60% basicity and no ultrasound. Notably, the results for titanium uniformity show an 18.5% increase with ultrasound for 60% basicity tanning liquor and a 12.5% increase for the 40% basicity level. The larger molecules in 60% basicity make it less efficient in penetration. Therefore, ultrasound can improve transport kinetics in the hide and load the tanning liquor with a greater number of smaller molecules through active sonic agitation-cavitation, leading to an overall enhancement in titanium distribution [10].

Table 5 Influence of Alkalinity of tanning solution on effectiveness of 30 kHz ultrasonic tanning

Parameters	**40% Alkalinity**		**60% Alkalinity**	
	With ultra sound	**Without ultrasound**	**With ultra sound**	**Without ultrasound**
Titanium oxide (TiO_2) in leather	18.35	17.25	17.60	17.21
Uniformity of titanium distribution, %	72.82	64.75	70.20	59.25
Shrinkage temperature, Ts, °C after basification	99.5	95.9	99.8	94.7

3.2.3. Pretreatment of titanium tanning liquor with ultrasound

Table 6 indicates that the strongest tanning performance was observed when ultrasound was applied in both the pretreatment (USP) and tanning (UST) steps. In contrast, the weakest tanning performance was observed when ultrasound was not used in either step. Interestingly, while ultrasound improved tanning effectiveness, the overall tanning performance of USP was somewhat worse than UST, as measured by all three performance indicators. Therefore, the most effective strategy for enhancing tanning effectiveness with ultrasound is to apply it both before tanning and during the tanning process (basification). Ultrasound enhances tanning effectiveness by generating a superior tanning agent during pretreatment, which allows for better penetration during tanning. It is unclear whether ultrasound promotes complexation between collagen and the tanning agent, but it is possible since ultrasound can promote chemical reactions. The importance of tanning agent penetration and collagen fixation (complexation) should be explained in this context. It is generally accepted that for leather dyeing, deeper penetration of the dyestuff into the hide results in a less colored surface of the leather [11].

Uneven tanning or wrinkled leather can result from a greater concentration of tanning agent on the surface, which leads to lower concentrations in the interior layers. To achieve more uniform tanning, it is important to minimize the difference in tanning agent content between the outer and inner layers. Ultrasound can enhance tanning effectiveness by promoting penetration, which is a necessary precursor to complexation [14]. Ultrasound can de-aggregate and reduce the effective size of titanium tanning agents, improving their penetration into the hide. Additionally, the cavitation effect of ultrasound can increase the translational energy of the tanning particles, making surface penetration more likely. This increased penetration can lead to greater titanium uptake, more uniform distribution of titanium, and a higher shrinkage temperature of the leather.

Table 6 Influence of pretreating titanium Tanning Liquor with 30 kHz ultrasound on titanium tanning

	Titanium oxide (TiO_2) in leather, %	**Uniformity of titanium distribution, %**	**Shrinkage temperature, Ts oC**
Pretreatment titanium Tanning with ultrasound (USP)	19.45	80.50	99.6
Ultrasound pretreatment Tanning (UPT)	19.65	82.60	100.5
Both pretreating titanium tanning liquor and tanning with the ultrasound (USP+UPT)	20.40	87.30	103.5
No Ultrasound (No US)	18.93	71.40	96.8

4. Conclusion

Ultrasound at 30 kHz frequency has been found to improve titanium tanning by enhancing penetration, improving distribution uniformity, and increasing the shrinkage temperature. The effects of 60 kHz ultrasound are minimal compared to those of 30 kHz ultrasound at the same intensity. The benefits of ultrasound are more noticeable when using low dosage (5% TiO_2 offer) and high basicity (60%) of titanium tanning solution, rather than high dosage (10%) and low alkalinity (40%). Ultrasound has been found to enhance tanning effectiveness, with the combination of ultrasonic pretreatment and tanning resulting in the strongest treatment effect and a leather shrinkage temperature of 107.9 ^{o}C. These improvements are likely due to the de-aggregation of titanium tanning agent species in the liquor and increased mass transport of these species into the hide due to cavitation-induced translational energy increases. Further research into the use of ultrasound in tanning (and hide processing more broadly) is warranted.

Compliance with ethical standards

Acknowledgments

The authors are grateful to Bahri University for support and national Centre for research for giving the possibility to use the resources and facilities of their laboratory.

Disclosure of conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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