DEVELOPMENT OF PROCESSES IN THE USE OF PEROXIDE AS AN INGREDIENT TO REDUCE FREE FORMALDEHYDE LEVELS IN THE SKIN

Emiliana ANGGRIYANI*, Laili RACHMAWATI, Nais Pinta ADETYA

Department of Leather Processing Technology, Politeknik ATK Yogyakarta, Sewon, Bantul, 55281 Yogyakarta, Indonesia, emiliana.anggry@gmail.com

Received: 13.01.2020 Accepted: 22.05.2020 https://doi.org/10.24264/lfj.20.2.6

DEVELOPMENT OF PROCESSES IN THE USE OF PEROXIDE AS AN INGREDIENT TO REDUCE FREE FORMALDEHYDE LEVELS IN THE SKIN

ABSTRACT. This study aims to reduce the levels of free formaldehyde in the skin. The material used is goat skin. The process is carried out by formaldehyde (formalin) tanning on pickled goat skin. Furthermore, skin that has been tanned with formalin is washed with peroxide (H_2O_2) 0.5%, 1% and 2%. The formalin tanned skin produced was tested for formalin levels contained in the skin, then the data obtained was analysed by One Way ANOVA test. In addition, physical tests were carried out for the average value of tear strength and softness. The results showed that the higher the level of H_2O_2 used, the smaller the formalin content in the skin. The best results were obtained using 1% H_2O_2 which was 0.12 ± 0.005 % (p <0.05) taking into account the safety aspects of H_2O_2. Furthermore, free formaldehyde levels of 0.045 mg/kg were obtained at 1% H_2O_2. The value of tear strength with formaldehyde is higher than that of chrome tanning while the softness value is still below that of chrome tanning. Therefore, the use of H_2O_2 can be considered in an effort to reduce the levels of formaldehyde contained in formaldehyde as an alternative tanner substitute for chrome minerals.

KEY WORDS: reduce, formaldehyde, peroxide, skin

DEZVOLTAREA UNOR PROCESE DE UTILIZARE A PEROXIDULUI CA INGREDIENT PENTRU REDUCEREA NIVELULUI DE FORMALDEHIDĂ LIBERĂ ÎN PIELE

REZUMAT. Acest studiu își propune reducerea nivelului de formaldehidă liberă din piele. Materialul folosit este pielea de capră. Procesul se realizează prin efectuarea tăbăcirii cu formaldehidă (formalină) pe piele de capră piclată. Mai mult, pielea care a fost tăbăcită cu formalină este spălată cu 0,5%, 1% și 2% peroxid (H_2O_2). Pielea tăbăcită cu formalină obținută a fost testată pentru a determina nivelurile de formalină conținută în piele, apoi datele obținute au fost analizate prin testul One Way ANOVA. În plus, s-au efectuat teste fizico-mecanice pentru a determina valoarea medie a rezistenței la sfâșiere și moliciunea. Rezultatele au arătat că, cu cât este mai mare nivelul de H_2O_2 utilizat, cu atât conținutul de formalină este mai mic în piele. Cele mai bune rezultate s-au obținut utilizând H_2O_2 în proporție de 1%, și anume 0,12 ± 0,005% (*p* <0,05), ținând cont de aspectele de siguranță ale H_2O_2. Mai mult, s-au obținut concentrații de formaldehidă liberă de 0,045 mg/kg la utilizarea H_2O_2 în proporție de 1%. Valoarea rezistenței la sfâșiere a pielii cu conținut de formaldehidă este mai mare decât cea pentru pielea tăbăcită în crom, în timp ce valoarea moliciunii este încă sub cea obținută pentru pielea tăbăcită în crom. Prin urmare, se poate lua în considerare utilizarea H_2O_2 în efortul de a reduce nivelurile de formaldehidă ca o soluție alternativă de tăbăcire pentru utilizarea cromului.

CUVINTE CHEIE: reducere, formaldehidă, peroxid, piele

DÉVELOPPEMENT D'UN PROCÉDÉ D'UTILISATION DU PEROXYDE COMME INGRÉDIENT POUR RÉDUIRE LES NIVEAUX DE FORMALDÉHYDE LIBRE DANS LA PEAU

RÉSUMÉ. Cette étude vise à réduire les niveaux de formaldéhyde libre dans la peau. Le matériau utilisé est la peau de chèvre. Le processus est effectué par le tannage au formaldéhyde (formol) sur la peau de chèvre picklée. De plus, la peau tannée au formol est lavée au peroxyde (H_2O_2) en proportion de 0,5%, 1% et 2%. La peau tannée au formol a été testée pour déterminer les niveaux de formol contenus dans la peau, puis les données obtenues ont été analysées par le test One Way ANOVA. De plus, des tests physiques ont été effectués pour déterminer la valeur moyenne de la résistance à la déchirure et de la douceur. Les résultats ont montré que plus le niveau de H_2O_2 utilisé était élevé, plus la teneur en formol de la peau était faible. Les meilleurs résultats ont été obtenus en utilisant 1% de H_2O_2 qui était de 0,12 ± 0,005% (*p* <0,05) en tenant compte des aspects de sécurité de H_2O_2. De plus, on a obtenu des niveaux de formaldéhyde libre de 0,045 mg/kg en utilisant 1% de H_2O_2. La valeur de la résistance à la déchirure avec le formaldéhyde est supérieure à celle du tannage au chrome tandis que la valeur de douceur est toujours inférieure à celle du tannage au chrome. Par conséquent, l'utilisation de H_2O_2 peut être envisagée dans le but de réduire les niveaux de formaldéhyde comme solution de tannage alternatif aux minéraux de chrome.

MOTS CLÉS : réduire, formaldéhyde, peroxyde, peau

** Correspondence to: Emiliana ANGGRIYANI, Department of Leather Processing Technology, Politeknik ATK Yogyakarta, Jl. Ringroad Selatan, Glugo, Panggungharjo, Sewon, Bantul, 55281, Yogyakarta, Indonesia, emiliana.anggry@gmail.com*

INTRODUCTION

The tanning process is a process that converts raw skin into finished skin to be used as raw material for making leather products. The leather tanning process consists of beam house operation, tanning, post tanning and finishing processes. These processes use various kinds of chemicals. Chemicals used in the tanning process should be environmentally friendly materials that are safe to use and safe for the environment. During this time the tanning process with chrome tanning materials is widely used to produce quality products. On the one hand, the use of chrome tanning material must be reduced from time to time because of the side effects of its use.

Some previous studies mention that chromium can damage the environment, is carcinogenic. Carcinogenic risk of chrome is due to the formation of Cr (VI) from Cr (III), therefore the first step that can be done is to reduce the formation of Cr (VI). [1] Vegetable material used in the retanning process can reduce the formation of Cr (VI) because the vegetable contains phenol compounds which will be oxidized first if there are free radicals or oxidizing agents. In addition to preventing the formation of hazardous compounds, another thing that can be done to form a better environment is to reduce the use of chrome as a tanning agent. Therefore, its use must be really considered, to maintain a better environmental sustainability. Much research has been done to be able to replace the chrome tanning material as a tanner material with good quality, of course, with existing developments.

The use of non-chrome tanning agents is very necessary in the context of substitution for the tanning process. One of the ingredients that can be used is formalin tanning material for garment articles. The use of tanning agents in the future can be developed for chrome substitution. However, based on international regulations the final leather product should have maximum ≤ 75 mg/kg of free formaldehyde content.

The common source of free formaldehyde found in leathers comes from tanning or retanning agents. Unreacted free formaldehyde becomes the primary source of formaldehyde detected in the leather. One of the desirable processes for aldehyde-tanned leather to reduce the formaldehyde content that have been studied is the modification of glutaraldehyde with polyurethane surfactant mixture solutions at different times. The formaldehyde content of mixture solution decreased by 5% when the solution mixed an hour later [2].

The use of formaldehyde as tanning agent, it is necessary to consider the presence of formaldehyde in the skin. Therefore it is important to reduce the presence of formaldehyde content in leather [3]. Taking advantage of the ability of polyphenols from vegetables to reduce the formaldehyde content of leathers treated with formaldehyde resins is an excellent example of clean technology in the tannery sector, especially given the known harmful nature of formaldehyde. Such measures help to achieve a more sustainable leather industry.

The decrease in the formaldehyde content in leather retanned with formaldehyde synthesized resins by the dyeing process could be explained by the reaction between formaldehyde and the amino groups present in the dyes structure. It should be noted that the extent of this decrease is a function not only of the number of the amino groups present in the dyes but also of their relative reactivity with formaldehyde. The vicinity of other functionalities, such as –OH, -N=N- and $-NO_2$, to the amino groups can lead to the formation of relatively stable cyclic structures mediated by hydrogen bonds. When this occurs, the reactivity of this amino group with formaldehyde can decrease [4].

In addition to the availability of chrome substitutes, the thing to think about is the quality of the skin produced. Because after all the skin produced must have certain standards to be sold. Testing the physical quality of the skin must be considered in order to achieve the desired skin standard.

The existence of complaints of environmental security due to the use of chrome tanning materials encourage the search for chromic substitution materials, which can provide quality that resembles chrome tanned leather. This is of course by still paying attention to the safety standards for the use of these substitutes, in this case formaldehyde. Formaldehyde can be used as long as it can meet skin safety standards.

EXPERIMENTAL

Materials and Methods

Instruments

Drum process, knife, pH indicator, bucket, and scales.

Materials

6 pickle goats skin (5 SqFt/ 0,6 mm), formalin 70%, NaCl, water, wetting agent (Peramit MLN, Pulcra chemicals), Acid batting (Feliderm Bat AB, Stahl), Bleaching agent (NaOCl, Brataco), Oxalic acid, $NaHCO_3$, Na-Formate, H_2O_2, Na-Bisulfit, dispersing agent (Coralon OT, Stahl), syntan (Tanicor PWB, Stahl), acrylic (Tergotan ESN, Stahl), sulphited oil (Derminol ASN, Stahl), Formic Acid, and fungicide (Preventol Cr, Lanxess).

Tanning Process

The tanning process is carried out by pretanning on pickle goat skin using formaldehyde, then washing with peroxide at the presentation of 0.5%, 1% and 2%. Then proceed with tanning using a replacement tanning agent (syntan).

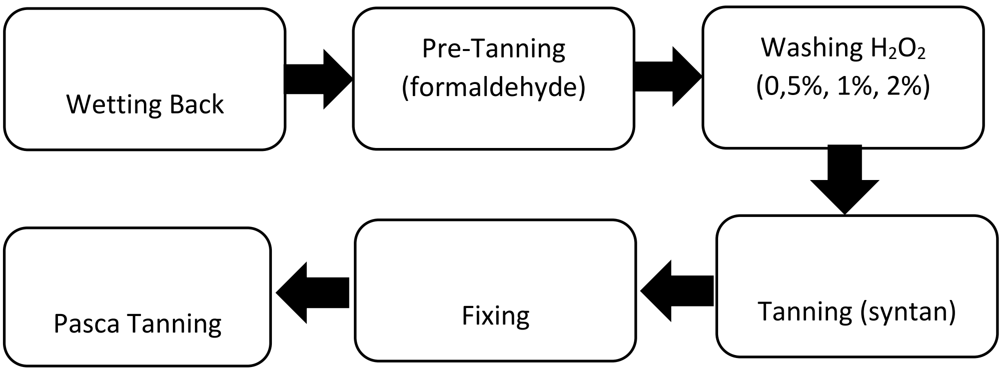

Figure 1. Tanning Process Diagram

Data Analysis

The results obtained (after fixing) were analyzed by the Different Test ANOVA, then continued with Independent Sample T-Test using the SPSS statistical 22 IBM. Further results from crust skin were analyzed using FTIR (Fourier Transmitted Infra Red). Furthermore, crust skin was also tested organoleptically to determine the value of tear strength and softness.

RESULTS AND DISCUSSIONS

Formaldehyde Content

The bound Formalin content contained in the skin decreases when washing by using H_2O_2 (peroxide) starting from 0.5%, 1% and 2% as shown in Table 1. This shows that the higher the percentage of peroxide used in the end of tanning can reduce bound formalin levels detected. Results in Table 1 show that there was a significant difference (P <0.05) between 0.5%, 1% and 2% peroxide use. Whereas between 1% and 2% peroxide use there was no significant difference (Independent Sample T-Test). Therefore, the best results used to produce the lowest formalin levels are enough to use 1% peroxide.

Table 1: Formaldehyde content on skin

H_2O_2 level	Formaldehyde level (%)
0.5%	0.23 ± 0.01^a
1%	0.12 ± 0.005^b
2%	0.11 ± 0.0^b

*Different superscript shows the significance different (P<0.05)

Skins with 1% H_2O_2 were tested for free formaldehyde levels and 0.045 mg/kg was the average result (meet the standard on Table 2). Important reductions in the formaldehyde content of formaldehyde resin-treated leathers by the action of adequate scavengers will result in a more sustainable tanning industry not only from the environmental point of view but also from a human health viewpoint, given the carcinogenic character of formaldehyde. This carcinogenic character fully justifies the application of the adequate formaldehyde scavengers in industrial processing of leather, textiles and construction materials [5].

Table 2: Free Formaldehyde content standards [6]

Countries/standards	Free formaldehyde content (mg/kg)		
	Articles for babies	Skin contact products	Not contact by skin
China	≤20	≤75	≤300
European Union	≤20	≤75	≤200
America	≤20	≤75	≤300
Japan	≤20	≤75	≤300
Okeo-Tex Standard 100	≤20	≤75	≤300
OKO Tex	≤20	≤75	≤300
SG Mark	≤50	≤75	≤150
ECO-Tex Standard 100	≤75		≤300
Australia	≤100		≤1500

The most dominant reaction between formaldehyde and skin protein is the skin amine group from the amino acid lysine. The reaction between amines and formaldehyde forms a formation called methylol derivatives [7]. The bond between the skin amine group and the aldehyde as shown in Figure 2.

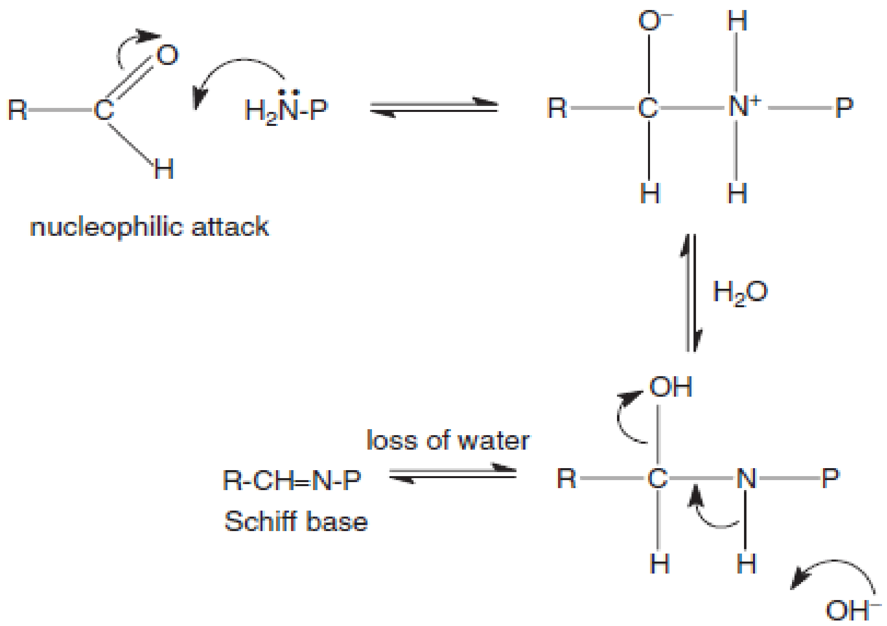

Figure 2. Aldehyde reaction with an amino group of skin proteins (P = protein) [8]

Apart from using peroxide on decrease formaldehyde content, gallic acid can be used [5]. When the presence of formaldehyde in leather is expected, gallic acid is a good option either in the final washing of the leather production process or as an alternative to formic acid as final fixing agent since it causes a marked reduction in the formaldehyde content. In most of the treatments with gallic acid, the formaldehyde content in treated leathers was below the limit for goods that are in direct contact with skin (65-75 mg/kg).

The values of formaldehyde reduction are somewhat higher due to the greater amount of mimosa extract applied. The change in the formic acid by the gallic acid as fixing agent resulted in a reduction of formaldehyde content that grew from 60% to 85%. This reduction was even more pronounced if together with the effect of fixing with gallic acid, the action of the mimosa extract in the retanning process was considered. The effect of gallic acid in reducing the formaldehyde content in split leather retanned with melamine formaldehyde resin was more intense and occurred more quickly than that of the mimosa extract, probably due to the greater number of –OH groups amenable to reaction with formaldehyde in the gallic acid offered than in the mimosa extract. Therefore, gallic acid is suitable as formaldehyde scavenger in the leather industry, although further experiments should be carried out to check its effect on fastness properties (mainly to light and temperature) and leather shades [5].

Formalin is a toxic material that is harmful to the environment and health. Formalin can be used as tanning agent because it contains formaldehyde. Formaldehyde is one of the simple aldehyde tanners. Formaldehyde when used as tanning agent can produce white skin (wet white leather).

Formaldehyde has been used as a tanning agent and as a means of hardening proteins for many years. It is a remarkable tanning material that usually has its practical application as an adjunct to some other tanning agent. The predominant reaction between formaldehyde and hide protein is generally accepted to be with the amino acid, lysine. This is a typical amine-formaldehyde reaction with the formation of the methylol derivatives [7]. The tannage yields leather with shrinkage temperature up to 80°C [8].

Global warming or the issue of “climate change” is pushing for a greener or cleaner industry both for leather, textile and paper processing. Green technology for chrome-free tanning based on D-Lysine GTA has been developed. In the formaldehyde reaction with proteins, the first to be attacked is the amine group in the Lysine position between the polar groups of the peptide. The physicochemical properties of the skin are improved with respect to texture, hydrothermal stability, mechanical strength, resistance to collagenolytic activity, and also organoleptic properties [9]. The amino groups both lysine and hydroxyproline are involved in the glutaraldehyde tanning reaction. It is possible that D-Lysine has improved hydrothermal stability. Increased wrinkle temperature indicates increased stability of wet white skin [9].

The skin which is retouched with formaldehyde resin is then retreated with vegetable polyphenol components, indicating that the formaldehyde content in the skin produced is maintained below 16 mg/kg [3]. States that the formalin content in the skin is reduced by adding grape seed extract to the process of retanning [10].

Table 3: Physical characteristics of goat crust

Treatment	Tear strength (kg/cm)	Softness (mm)
Tanning formaldehyde (without washing)	34.81	4.2
Tanning formaldehyde (washing with peroxide)	29.27	4.27
Chrome tanning	24.52	6.37

Based on Table 3 it can be seen that tanning leather with formalin is able to produce crust leather with higher tear strength than chrome tanning for garment articles. While from the softness level, crust skin tanned using formalin is still low compared to chrome tanning. Tear strength without washing has a higher yield because free formalin is still contained in the skin, so the level of material strength in the skin is stronger than after washing with peroxide. However, the effects produced from the skin without washing formalin are less recommended, because there are certain standards that must be met by each skin product for tolerance of the formaldehyde content in the skin.

The main advantages of chrome tanning are high speed, low cost, light color, and excellent preservation of the hide protein. Chrome tanning rapidly took its place in the commercial world shortly after its discovery and became the most common method of tanning light leather [7].

Excessive formaldehyde should be removed by washing in order to avoid callouses on the grain. A further disadvantage consists in the increased water-absorption of leathers treated with formaldehyde. However, a pure white colour of leather and a fine, closed appearance of grain are obtained [11].

In the tanning process using formaldehyde, a cross-linking occurs that forms a covalent bond between the aldehyde group (-CHO) with the NH_2^+ group of the amino acids glycine, proline and hydroxyproline that form bonds with triple helix in skin collagen. However, the bond is lower because in formaldehyde the absorbability of the tanned material is not strong enough compared to the chromium tanning material which has a stronger absorption to form complex bonds [11].

FTIR Analysis

FTIR analysis of the sample is shown in Figure 3. Goat skin has several characteristic absorption bands. Strong bands at absorption of 1451 cm^{-1} are characteristic of aromatic rings (C-C and C-H), while secondary C-O alcohol vibrations are at 1087 cm^{-1} [12]. The alkyne absorption band C = C is shown as a strong band in the wave region 1500-1675 cm^{-1} [13]. When viewed from the absorption of infrared radiation, there is no significant change between the absorption bands of the skin before and after washing with peroxide. However, there is a slight difference in the skin sample without the peroxide washing process (0% H_2O_2) where the C=N bond is still detected through absorption bands in the wave number region 1547-1551 cm^{-1} [12]. While in the process of washing peroxide 0.5%; 1% and 2%, the band size in the C=N bond constricts with increasing peroxide concentration.

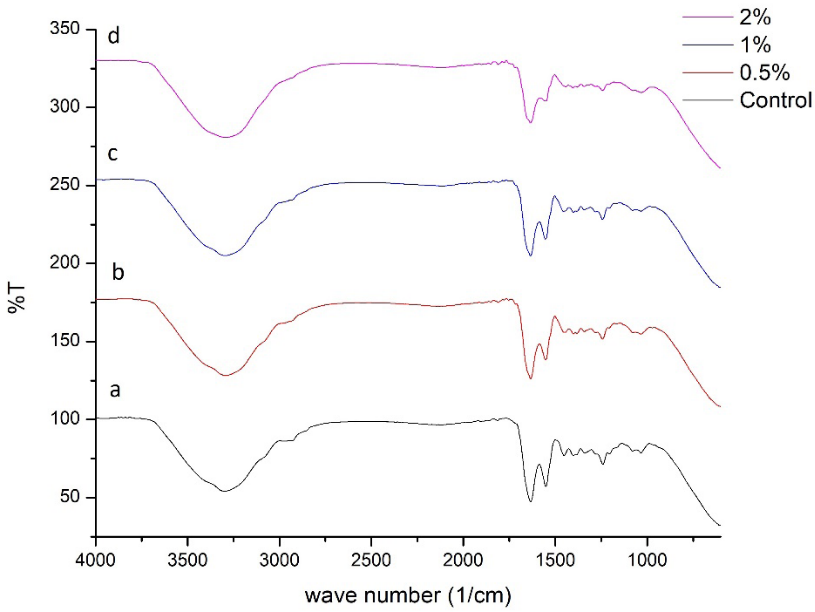

Figure 3. FTIR spectra of goat skin with various H_2O_2 concentrations used in washing process (a) 0%; (b) 0.5%; (c) 1% and (d) 2%

Figure 3 shows the FTIR spectrum of goat skin with various concentrations of peroxide used in the washing process. Strong bands at 1653 cm^{-1} are characteristic of C=O stretching vibrations around 1650-1900 cm^{-1}. Schiff bases are formed due to the reaction between aldehyde bonds and amino groups. The functional group in this compound is the carbonyl group, C=O. The presence of hydrogen atoms makes aldehydes very easily oxidized. Aldehydes can be easily oxidized using all types of oxidizing agents [14]. Hydrogen peroxide (H_2O_2) is an inorganic chemical that has strong oxidizing properties. One of the advantages of hydrogen peroxide compared to other oxidizing agents is that it is environmentally friendly because it does not leave harmful residues [15].

Goat skin washed with 2% peroxide has the sharpest O-H vibrations. This shows that this sample has the most amount of O-H. These results illustrate that hydrogen bonds that are bound to amino groups form stable structures. When this occurs, the reactivity of this amino group with formaldehyde can decrease [5]. The hydrogen bond increases for the oxidation of C-OH to C = O, this is known from the change in the O-H band around 2500-3300 cm^{-1} which is increasingly swooping with the addition of H_2O_2 concentration (Figure 3). Therefore, the optimal concentration of peroxide used is 2%.

CONCLUSIONS

The use of H_2O_2 of 1% can be used to reduce the content of formalin bound in tanned skin using formaldehyde. Tanning with formaldehyde tanning material can produce higher tear strength compared to chrome tanning material.

The use of formaldehyde as a tanning agent must still be considered and further developed for future research. This is because there are still a number of things that remain uncertain regarding environmental regulations, in addition to the formalin tanning material must be considered regarding its usefulness for various types of articles as a substitute for chrome.

REFERENCES

1. Anggriyani, E., Nugroho, A.R., Rosiat, N.M., Technology of reducing Cr(VI) on leather processing using mimosa as retanning agent, *Leather and Footwear Journal*, **2019**, 19, 1, 67–72, https://doi.org/10.24264/lfj.19.1.8.
2. Sun, X., Jin, Y., Lai, S., Pan, J., Du, W., Shi, L., Desirable retanning system for aldehyde-tanned leather to reduce the formaldehyde content and improve the physical-mechanical properties, *J Clean Prod*, **2018**, 175, 199–206, https://doi.org/10.1016/j.jclepro.2017.12.058.
3. Marsal, A., Cuadros, S., Manich, A.M., Izquierdo, F., Font, J., Reduction of the formaldehyde content in leathers treated with formaldehyde resins by means of plant polyphenols, *J Clean Prod*, **2017**, 148, 518–526, https://doi.org/10.1016/j.jclepro.2017.02.007.
4. Marsal, A., Cuadros, S., Cuadros, R.M., Font, J., Manich, A.M., Dyestuffs and formaldehyde content in split leather treated with formaldehyde resins, *Dyes Pigm*, **2018**, 158, 50–59, https://doi.org/10.1016/j.dyepig.2018.05.027.
5. Marsal, A., Cuadros, S., Ollé, L., Bacardit, A., Manich, A.M., Font, J., Formaldehyde scavengers for cleaner production: A case study focused on the leather industry, *J Clean Prod*, **2018**, 186, 45–56, https://doi.org/10.1016/j.jclepro.2018.03.109.
6. Wang, X., Yan, Z., Liu, X., Qiang, T., Chen, L., Guo, P., Yue, O., An environmental polyurethane retanning agent with the function of reducing free formaldehyde in leather, *J Clean Prod*, **2019**, 207, 679–688, https://doi.org/10.1016/j.jclepro.2018.10.056.
7. Thorstensen, T., Practical Leather Tehnology, 4rd ed. Florida, New York: Robert E. Keiger Publishing Company Malabar, **1993**.
8. Covington, A., Tanning Chemistry: The Science of Leather, Northampton: Royal Society of Chemistry, **2009**.
9. Krishnamoorthy, G., Sadulla, S., Sehgal, P.K., Mandal, A.B., Greener approach to leather tanning process: D-Lysine aldehyde as novel tanning agent for chrome-free tanning, *J Clean Prod*, **2013**, 42, 277–286, https://doi.org/10.1016/j.jclepro.2012.11.004.
10. Bayramoĝlu, E.E., Hidden treasure of the nature: PAs. The effects of grape seeds on free formaldehyde of leather, *Ind Crops Prod*, **2013**, 41, 1, 53–56, https://doi.org/10.1016/j.indcrop.2012.03.040.
11. John, G., Possible Defects in Leather Production, Lampertheim: Europaring 24 D-68623, **1996**.
12. Baker, M.J., Trevisan, J., Bassan, P., Bhargava, R., Butler, H.J., Dorling, K.M., Fielden, P.R., Fogarty, S.W., Fullwood, N.J., Heys, K.A., Hughes, C., Lasch, P., Martin-Hirsch, P.L., Obinaju, B., Sockalingum, G.D., Sule-Suso, J., Strong, R.J., Walsh, M.J., Wood, B.R., Gardner, P., Martin, F.L., Using Fourier transform IR spectroscopy to analyze biological materials, *Nat Protoc*, **2014**, 9, 8, 1771–1791, https://doi.org/10.1038/nprot.2014.110.
13. Canals Parello, T., Morera Prat, J.M., Combalia Cendra, F., Bartoli Soler, E., Application of Infrared Spectroscopy (FTIR and NIR) in Vegetable Tanning Process Control, *J Soc Leath Tech Ch*, **2013**, 97, 93–100.
14. Wang, X., Ren, L., Qiang, T., Novel Way of Transformation of Tannery Waste to

Environmentally Friendly Formaldehyde Scavenger, *Environ Prog Sustain Energy*, **2019**, 28, 2, 285–290, https://doi.org/10.1002/ep.10329.

15. Al Zoubi, W., Ko, Y.G., Organometallic complexes of Schiff bases: Recent progress in oxidation catalysis, *J Organomet Chem*, **2016**, 822, 173–188, https://doi.org/10.1016/j.jorganchem.2016.08.023.