TESTING A NEW PRODUCT BASED ON ESSENTIAL OIL WITH ANTIFUNGAL PROPERTIES FOR TREATMENT OF NATURAL LEATHER

Olga NICULESCU*, Luminiţa ALBU, Gheorghe COARĂ, Lucreţia MIU, Carmen GAIDĂU, Rodica CONSTANTINESCU, Dana GURĂU

INCDTP – Division Leather and Footwear Research Institute, 93 Ion Minulescu St., Sector 3, Bucharest, Romania

Received: 09.07.2019 Accepted: 23.09.2019 https://doi.org/10.24264/lfj.19.3.6

TESTING A NEW PRODUCT BASED ON ESSENTIAL OIL WITH ANTIFUNGAL PROPERTIES FOR TREATMENT OF NATURAL LEATHER

ABSTRACT. Tanned, crust or finished leather may be damaged by different types of molds, which irreversibly degrade natural leather (during processing or storage). This paper presents the resistance to *Aspergillus niger* strain of leather samples treated with the developed cinnamon essential oil-based product. Testing of antifungal product based on cinnamon oil was carried out monitoring the manner in which mold growth is influenced by the treatment applied to the sample through the resistance to mold in simulated contamination conditions. This product improves leather and leather product resistance to fungi, while ensuring a higher quality of natural leathers.

KEY WORDS: cinnamon essential oil, natural leather, *Aspergillus niger*

TESTAREA UNUI NOU PRODUS PE BAZĂ DE ULEI ESENȚIAL CU PROPRIETĂȚI ANTIFUNGICE PENTRU TRATAREA PIEILOR NATURALE

REZUMAT. Atât pieile tăbăcite, cât și cele crust sau finisate pot fi deteriorate de diferite tipuri de mucegaiuri, care degradează în mod ireversibil pielea naturală (în timpul prelucrării sau depozitării). Această lucrare prezintă rezistența la tulpina de *Aspergillus niger* a probelor de piele tratate cu produsul dezvoltat pe bază de ulei esențial de scorțișoară. Testarea produsului antifungic pe bază de ulei esențial de scorțișoară s-a realizat prin monitorizarea modului în care creșterea mucegaiului este influențată de tratamentul aplicat pe probă prin rezistența la mucegai în condiții de contaminare simulată. Acest produs îmbunătățește rezistența pielii și a produselor din piele la fungi, asigurând o calitate mai înaltă a pieilor naturale.

CUVINTE CHEIE: ulei esențial de scorțișoară, piei naturale, *Aspergillus niger*

ESSAI D'UN NOUVEAU PRODUIT À BASE D'HUILES ESSENTIELLES AUX PROPRIÉTÉS ANTIFONGIQUES POUR LE TRAITEMENT DU CUIR NATUREL

RÉSUMÉ. Les cuirs tannés, en croûte ou finis peuvent être endommagés par différents types de moisissures, qui dégradent de manière irréversible le cuir naturel (pendant le traitement ou le stockage). Cet article présente la résistance à la souche d'*Aspergillus niger* d'échantillons de cuir traités avec le produit développé à partir d'huile essentielle de cannelle. Le test du produit antifongique à base d'huile essentielle de cannelle a été réalisé en contrôlant l'influence de la croissance de moisissures sur le traitement appliqué à l'échantillon par la résistance à la moisissure dans des conditions de contamination simulées. Ce produit améliore la résistance du cuir et des produits en cuir aux moisissures, assurant une meilleure qualité du cuir naturel.

MOTS CLÉS : huile essentielle de cannelle, cuir naturel, *Aspergillus niger*

INTRODUCTION

Tanned, crust or finished leather may be damaged by different types of mold from the *Aspergillus niger*, *Aspergillus flavus*, *Trichoderma viride*, *Penicillium glaucom*, *Penicillium cyclopium* and *Paecilomyces variotii* species, which, by means of the enzymes they produce (colagenases, lipases and proteases), irreversibly degrade natural leather (during processing or storage). Biocides used in the leather industry are toxic to humans and the environment, some of which are prohibited by the directives in force (pentachlorophenol, polyhalogenated phenolic compounds) [1]. Recent research aims to fully or partially replace potentially toxic biocides with environmentally friendly materials. In the past years, natural antimicrobial agents, such as essential oils, have been identified and used in the treatment of natural leather. The literature indicates the use of oregano, aloe vera, eucalyptus, lavender, coriander or cedar essential oils to treat tanned leather in wet finishing operations, in the composition of the fatliquoring mixture or for surface treatment [2-8]. Essential oils are highly concentrated in biologically active compounds with different properties: antiseptic, antibacterial, immunostimulatory etc. [9, 10]. These can be used to protect against damage caused by fungi and bacteria. The composition of cinnamon essential oil, analysed by gas chromatography coupled with mass spectrometry – GC-MS, indicates the presence of the following compounds: Eugenol – 85.07%, Caryophillene – 5.28%, Linalool – 1.85%, alpha-Pinene – 1.31%, Phellandrene – 1.59%, Benzyl Benzoate – 1.48% etc. [11, 12]. The effectiveness of biocides is established using biological methods of assessing mold and bacteria attack on leather. Assessment is performed using standardized, leather-specific methods [13].

EXPERIMENTAL

Materials

• Product (marked P-SC) with antifungal properties (made from cinnamon essential oil, ethanol, non-ionogenic emulsifier, polyethylene glycol 400 and deionized water): dry substance – 18-22%, pH (10% solution) – 5-5.5, density – 0.920-0.950 g/cm^3 (INCDTP – Division Leather and Footwear Research Institute Bucharest, Romania).

• Ethanol (Chemical Company, Germany), density – 0.789 g/cm^3 at 20°C, boiling point – 78°C, melting point – 114°C, water solubility – in any proportion.

• The crust bovine leathers natural grain assortments, mineral tanned and wet finished by retanning, fatliquoring and dyeing (1.2-1.4 mm thick, dyed brown) (INCDTP – Division Leather and Footwear Research Institute Bucharest, Romania).

METHODS

• Bioassay was used to determine leather resistance to bacteria and fungi. Method for resistance to fungi is provided in STAS 12697/A91:2008 "Leather. Mold attack test". It examines how the growth of mold is influenced by existing treatment on the leather sample treated with biocides through mold resistance under simulated contamination.

Aspergillus niger spores were inoculated in 3 points (right, center and left of the sample) according to the procedure of ASTM D 4576-86, "Standard test method for mold growth resistance of blue stock (leather)". The duration of incubation is 28 days, fungal observations being made at intervals of 7, 14, 21 and 28 days. The development of *Aspergillus niger* strain on leather samples analyzed was expressed according to standard notation by ranking from 0 to 5 (0 – absence of stems and a strong fungitoxic effect, 5 – an almost non-existent effect, i.e. the mold covers the entire surface of the specimen).

• Optical microscopy images were captured using a Leica stereomicroscope S8AP0 model with optic fiber cold light source, L2, with three levels of intensity, and magnification 40X.

• Chemical characteristics of the uncoated leathers were determined according to the following standards: moisture (%) – SR EN ISO 4684:2006; extractable content (%) – SR EN ISO 4648:2008; chromium oxide content (%) – SR EN ISO 5398:2008.

• Chemical characteristics of antifungal product based on cinnamon were determined according to the following standards: moisture (%) – SR EN ISO 4684:2006; pH 10% solution (units) – SR EN ISO 4698:2006; density (g/cm^3) – SR EN ISO 5397:1996. Testing of antifungal product based on cinnamon (P-SC) was carried out monitoring the manner in which mold growth is influenced by the treatment applied to the sample through the resistance to mold in simulated contamination conditions.

Technological variants for treating the crust bovine leathers natural grain assortments are shown in Table 1.

Table 1: Technological variants for treating the crust bovine leather, natural grain assortments

Sample	Composition of antifungal product	Treated leather assortments
P- SC 1	500 g/L product P-SC 50 g/L ethanol 450 g/L water	Crust brown bovine leather
P-SC 2	400 g/L product P-SC 40 g/L ethanol 560 g/L water	Crust brown bovine leather
P-SC 3	300 g/L product P-SC 30 g/L ethanol 670 g/L water	Crust brown bovine leather
P-SC 4	200 g/L product P-SC 20 g/L ethanol 780 g/L water	Crust brown bovine leather
M	0	Crust brown bovine leather

The product with antifungal properties can be applied on crust bovine leather (processed by the neutralization-retention-dyeing-fatliquoring operations), by surface finishing, as a final operation (after the mechanical processing operations - drying, polishing, setting out - using an amount of 20-50% essential oil-based product and 10% ethanol diluted in water 1:1. The moistening solution is evenly spread on the leather surface, using a plush textile material. This operation is repeated twice. Treatment with this product can be repeated at certain time intervals, and the process of application on the leather surface is easy to perform (in the case of leather stored for a longer period of time).

RESULTS AND DISCUSSIONS

Physical-Chemical Characteristics of Antifungal Product Based on Cinnamon Essential Oil

The prepared product, P-SC consists of yellowish white fluids, homogenous, with 18-22% dry substance, pH – 5.0-5.5, density – 0.920-0.950 g/cm^3.

Characterization by Chemical Analyses

Chemical characteristics of the uncoated hides used to obtain natural grain box bovine leather (crust) were determined in accordance with standard STAS 1619:1994 (Table 2).

Table 2: Chemical characteristics of natural grain box bovine leather (crust)

Sample/Characteristic	P-SC 1	P-SC 2	P-SC 3	P-SC 4	M	ST 1619:1994
Moisture, %	14.28	14.45	14.72	14.15	14.82	14-15
Extractable content, %	7.22	7.14	7.86	7.05	7.67	Max.8
Chromium oxide content, %	5.23	5.54	5.78	5.98	5.84	Min.3.5

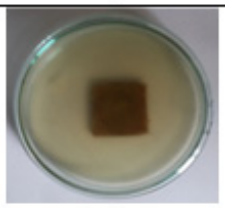
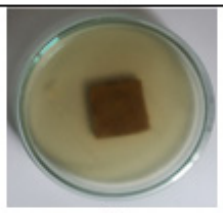
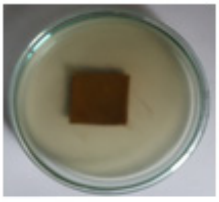
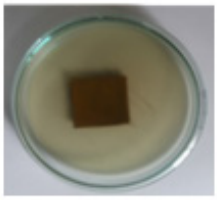
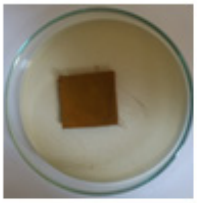
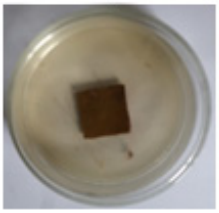
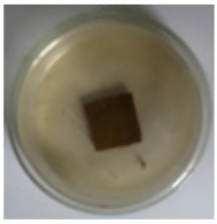
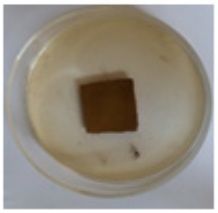
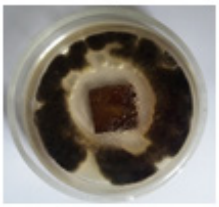
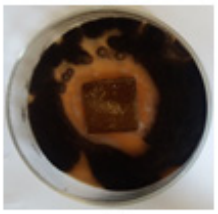
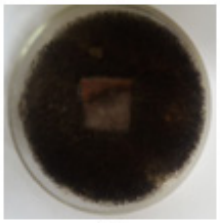
Chemical characteristics of the natural grain box bovine leather (crust) are within the limits specified in standard.

Biological Characterization of Obtained Leather Assortments

The samples treated with different amounts of antifungal product based on cinnamon oil,

P-SC, on the unfinished surface, were inoculated with biological material – *Aspergillus niger* spores. The goal was to monitor the influence of the treatment applied to the sample on mold growth through the mold resistance under simulated contamination, according to STAS 12697/A 91:2008. Development of the *Aspergillus niger* strain on leather samples over time, i.e. macroscopic images of the samples treated with antifungal product are shown in Table 3. The numbers under the images are the marks given according to the standard.

Table 3: Macroscopic images of samples treated with P- SC product after 7, 14 and 28 days

Sample/day	7	14	28
P-SC 1			
	0	0	0
P-SC 2			
	0	0	0
P-SC 3			
	0	0	0
P-SC 4			
	0	0	0
M			
	5	5	5

The most resistant to mold are leather samples (P-SC 1, P-SC 2, P-SC 3) treated with antifungal product (30-50% P-SC). The samples do not develop fungi for 28 days (mark 0). The sample P-SC 4 treated with antifungal product (20% P-SC) does not develop fungi for 28 days (mark 0), but mold develops around the leather sample treated with 20% P-SC.

The sample M (not treated with P-SC) develops mold in the first 7 days (mark 5).

CONCLUSIONS

- Essential oil isolated from cinnamon (*Cinnamomum verum*) containing: eugenol – 78.03%, aceteugenol – 10.93%, caryophylene – 9.46%.
- The samples treated with antifungal product (20-50% P-SC) do not develop fungi for 28 days (mark 0).
- The prepared antifungal and antibacterial product made from cinnamon essential oil, ethanol, non-ionogenic emulsifier, polyethylene glycol 400 and deionized water improves the resistance of bovine crust leathers to biological factors (fungi).
- The product P-SC can be used (in proportion of de 20-30%) in surface treatment of crust leathers (by dabbing with a textile cloth).

Acknowledgment

This publication is funded by the Minister of Research and Innovation through the Program 1 - Development of the National Research and Development System, Subprogram 1.2 - Institutional Performance - RDI excellence funding projects, Contract no. 6PFE/16.10.2018.

REFERENCES

1. Directive 2010/75/EU of the European Parliament and of the Council of 24 November **2010** on Industrial Emissions (Integrated Pollution Prevention and Control).
2. Bayramoglu, E.E., Unique biocide for the leather industry: essential oil of oregano, *J Am Leather Chem As*, **2007**, 102, 11, 347.
3. Cadirci, B., Basaran, B., Bitlisli, B., Yasa, I., Aslan, A., Physical and antimicrobial characteristics of aloe vera treated split suede leather, *J Am Leather Chem As*, **2010**, 105, 2, 34.
4. Sirvaityte, J., Siugzdaite, J., Valeika, V., Application of commercial essential oils of Eucalyptus and Lavender as natural preservative for leather tanning industry, *Rev Chim - Bucharest*, **2011**, 62, 9, 884.
5. Radwan, I.A., Abed, A.H., Abeer, M.R., Ibrahim, R.A., Abdallah, A.S., Effect of thyme, clove and cinnamon essential oils on Candida albicans and moulds isolated from different sources, *Am J Anim Vet Sci*, **2014**, 9, 4, 303-314, https://doi.org/10.3844/ajavsp.2014.303.314.
6. Niculescu, O., Leca, M., Moldovan, Z., Deselnicu, D.C., Obtaining and characterizing a product with antifungal properties based on essential oils and natural waxes for finishing natural leathers, *Rev Chim - Bucharest*, **2015**, 66, 11, 1733-1736.
7. Niculescu, O., Deselnicu, D.C., Georgescu, M., Nițuică, M., Finishing product for improving antifungal properties of leather, *Leather and Footwear Journal*, **2017**, 17, 1, 31-38, https://doi.org/10.24264/lfj.17.1.4.
8. Niculescu, O., Coara, G., Chelaru, C., Gurau, D., New Products Based on Essential Oils for Finishing Natural Leathers with Antifungal Performances–Part 2, The 7th International Conference on Advanced Materials and Systems ICAMS 2018 Bucharest, Romania, 18-20 October **2018**, Proceedings of The 7th ICAMS 2018, p. 281-286, https://doi.org/10.24264/icams-2018.V.4.
9. Romanian Pharmacopoeia (in Romanian), 10th edition, Medical Press, Bucharest, **1998**.
10. Council of Europe, European Pharmacopeia, vol. II, ESCOP Strasbourg, **2005**.
11. Moldovan, Z., Instrumental Analysis Methods, University of Bucharest Press, **2001**.

12. David, V., Medvedovici, A., Methods of separation and chromatographic analysis, University of Bucharest Press, **2008**.

13. ST 12697/A 91/2008, Standard for Determination of Leather Resistance to Fungi.