NEW PRODUCTS BASED ON ESSENTIAL OILS FOR FINISHING NATURAL LEATHERS WITH ANTIFUNGAL PERFORMANCES – PART 2

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Research aims the replacement of potentially toxic biocides with ecologic materials – essential oils extracted from plants. Some biocides used in the leather industry have a certain toxicity, and are prohibited by the directives in force. This paper presents the resistance to mold of leather treated with the developed essential oil-based products, development of the *Aspergillus niger* strain on leather samples over time, i.e. macroscopic images of the samples treated with antifungal products based on cedar and coriander oils. Because the product made of cedar essential oil is less efficient, mixtures of the two antifungal products (based on cedar and coriander oils) were used on the surface leather in the final dressing composition. Testing of antifungal products based on cedar and coriander oils 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. These products improve leather and leather product resistance to fungi, while ensuring a higher quality of leather objects.

Keywords: natural leathers, essential oils, *Aspergillus niger*

INTRODUCTION

In order to prevent the emergence and growth of microorganisms, biocides are used in various stages of leather processing, improving resistance to biological attack and preventing deterioration of mechanical and chemical properties of leather (Heidemann, 1994; Chirita *et al*., 1999; Niculescu *et al*., 2013; Niculescu *et al*., 2015).

Biocides (based on beta-naphthol, benzothiazole and sulfone derivatives, organic sulfur compounds, etc.) used in the leather industry have a certain toxicity to humans and the environment, some of which are prohibited by the directives in force (pentachlorophenol, polyhalogenated phenolic compounds) (Directive 2010/75/EU). Recent research aims to fully or partially replace potentially toxic biocides with environmentally friendly materials. The literature indicates the use of oregano, aloe vera, eucalyptus, lavender, or coriander essential oils to treat tanned leather in wet finishing operations, in the composition of the fatliquoring mixture or for surface treatment (Bayramoglu, 2007; Cadirci *et al*., 2010; Sirvaityte *et al*., 2011; Niculescu *et al*., 2017).

Essential oils are highly concentrated in biologically active compounds with different properties: antiseptic, antibacterial, immunostimulatory etc. (Romanian Pharmacopoeia, 1998; European Pharmacopeia, 2005). These can be used to protect against damage caused by fungi and bacteria. Cedar essential oil contains: thujopsene – 37.25% and cuparene – 9% with antibacterial and antifungal properties, cedrenol – 21% and cedrene – 20% with antimicrobial properties as main components (Moldovan, 2001; David *et al*., 2008).

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 (ST 12697/A 91/2008).

EXPERIMENTAL

Materials

Roda Wax MONO (Triderma, Germany), wax emulsion for ground coat: dry substance – 36.87%, pH (10% solution) – 4.2, Ford cup viscosity Φ4 – 12, kinematic viscosity, cSt – 8.97, density – 0.957 g/cm^3;

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Roda-Cryl 87 (Triderma, Germany), acrylic binder for ground coat, dry substance – 34.50%, pH (10% solution) – 6.0, Ford cup viscosity Φ4 – 14, density – 1.025 g/cm^3;

Roda-Pur Wx 1418 (Triderma, Germany) polyurethane binder for ground coat: dry substance – 19-21%, pH (10% solution) – 7.5-9.5.

Roda-Pur 5011 (Triderma, Germany), polyurethane binder used as a fixing agent (final dressing) for finishes applied to natural leather: dry substance – 40%, pH (10% solution) – 5.5, Ford cup viscosity Φ4 – 7, density – 1.053 g/cm^3.

Product (marked AF-C-2) with antifungal properties (made from cedar essential oil, beeswax, lanolin, ethanol and lauryl alcohol ethoxylated with 7 moles of ethylene oxide: dry substance – 11%, pH (10% solution) – 3.8, density –0.810 g/cm^3 (INCDTP– Division Leather and Footwear Research Institute Bucharest, Romania).

Product (marked AF-C-1) with antifungal properties (made from coriander essential oil, beeswax, lanolin, ethanol and lauryl alcohol ethoxylated with 7 moles of ethylene oxide: dry substance – 12%, pH (10% solution) – 4.5, density –0.820 g/cm^3 (INCDTP– Division Leather and Footwear Research Institute Bucharest, Romania).

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

Methods

Bioassay was used to determine the resistance to bacteria and fungi of leather. Method for resistance to fungi is provided in STAS 12697 / A 91: 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 was 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.

Testing of Antifungal Products Based on Cedar and Coriander Oils

The framework technology for dry finishing of bovine leather into natural grain box assortments, is presented in table 1.

Table 1. Framework technology for dry finishing of bovine hides into natural grain box

Operation	Dispersion composition/application method
Application of dispersion I (basecoat)	30 g/L aqueous wax emulsion (Roda wax MONO) 150 g/L aqueous acrylic dispersion (Roda-cryl 87) 150 g/L aqueous polyurethane dispersion (Roda-Pur Wx 1418) 670 g/L water Application by spraying (2 passes dispersion I)
Intermediate pressing	In hydraulic press with the mirror or fog plate, parameters: - temperature – 50-60^{o}C; pressure – 50-100 atm
Application of dispersion I	By spraying (2-3 passes dispersion I)

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Operation	Dispersion composition/application method
Application of final dressing (fixing)	Emulsion/dispersion with the following composition: 700 g/L aqueous polyurethane emulsion (Roda pur 5011) 20 g/L aqueous wax emulsion for handle 280 g/L water Application by spraying (2 passes final dressing)
Final pressing	In hydraulic press with the mirror plate, parameters: - temperature – 70-80°C; pressure – 50-100 atm.

Because the product made of cedar essential oil is less efficient, mixtures of the two antifungal products (AF-C-1, AF-C-2) were used on the surface leather in the final dressing composition.

Antifungal product based on coriander essential oil (AF-C-1) was obtained by the same method, using essential oil, wax emulsion, ethanol and ethoxylated lauryl alcohol.

Testing of antifungal products based on cedar (AF-C-2) and coriander oil (AF-C-1) 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.

Finished leathers were further treated with final dressing whose composition includes AF-C-2 and AF-C-1 products in various proportions (samples AF 1-AF 9) and leathers untreated with the products AF-C-2 and AF-C-1 (samples M1 and M2) (Table 2).

Table 2. Technological variants for treating bovine hides into natural grain box assortments

Sample	Final dressing composition	Treated leather assortments
AF 1	1000 g/L product AF-C-2	Film-coated brown box leather
AF 2	1000 g/L product AF-C-2	Uncoated brown box leather
AF 3	1000 g/L product AF-C-2	Film-coated black box leather
AF 4	1000 g/L product AF-C-2	Uncoated black box leather
AF 5	750 g/L product AF-C-2 250 g/L Roda pur 5011	Film-coated brown box leather
AF 6	750 g/L product AF-C-2 250 g/L Roda pur 5011	Uncoated brown box leather
AF 7	400 g/L product AF-C-1 400 g/L product AF-C-2 200 g/L Roda pur 5011	Film-coated brown box leather
AF 8	400 g/L product AF-C-1 400 g/L product AF-C-2 200 g/L Roda pur 5011	Film-coated black box leather
AF 9	400 g/L product AF-C-1 400 g/L product AF-C-2 200 g/L Roda pur 5011	Uncoated black box leather
M1	0	Film-coated brown box leather
M2	0	Uncoated brown box leather

RESULTS AND DISCUSSION

Biological Characterisation of the Obtained Leather Assortments

The samples treated with different amounts of antifungal product based on cedar oil, AF-C-2, and mixture of the two antifungal products (AF-C-1, AF-C-2), on the surface

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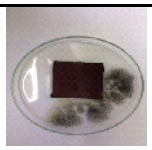
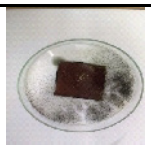
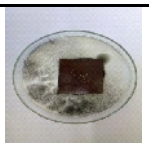
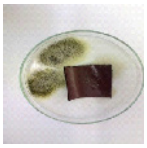
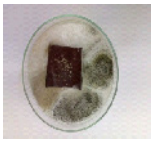
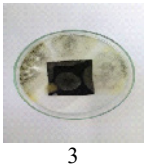
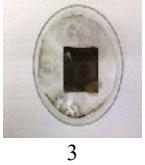
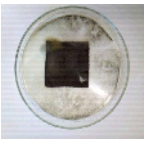
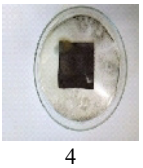
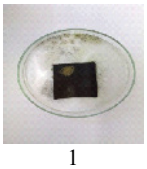
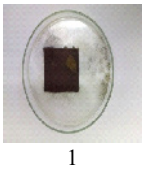
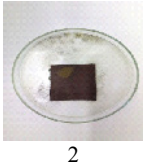
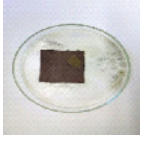
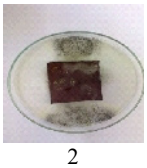
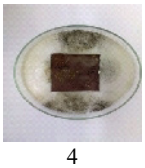
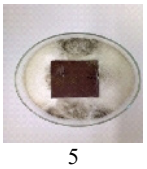
of unfinished and finished leather in the final dressing composition, were inoculated with biological material – *Aspergillus niger* spores.

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 9:2008 „Finished leathers. Mold resistance testing".

Aspergillus niger spores were inoculated in three areas: right side, center and left side of the sample, according to the procedure specified in ASTM D 4576-86 „Standard test method for mold growth resistance of blue stock (leather)". Incubation was 28 days, but observations were also performed at 7, 14 and 21 days. *Aspergillus niger* strain development was assessed by ranking: 0 – absence of stems and a strong fungitoxic effect, 5 – an almost non-existent effect (the mold covers the entire surface of the specimen).

Table 3. Macroscopic images of samples treated with AF-C-2 and AF-C-1 products after 7, 14, 21 and 28 days

Sample/ day	7	14	21	28
AF 1				
	0	2	2	3
AF 2				
	1	3	5	5
AF 3				
	3	3	4	4
AF 4				
	1	1	2	3
AF 5				
	2	4	5	5

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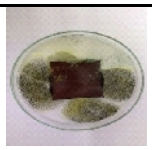
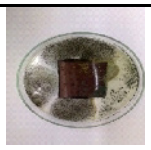
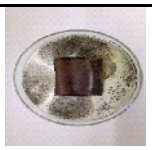
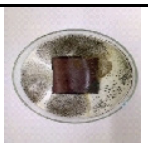
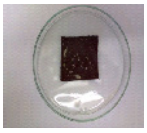
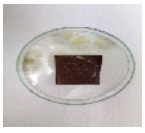
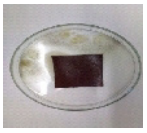
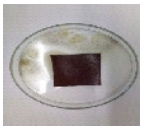
Sample/ day	7	14	21	28
AF 6				
	2	5	5	5
AF 7				
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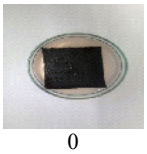
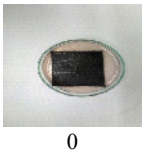
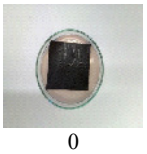
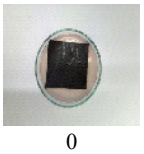
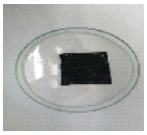
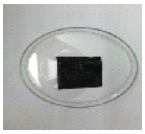
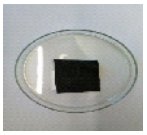
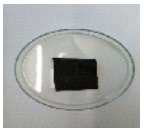
AF 8				
	0	0	0	0
AF 9				
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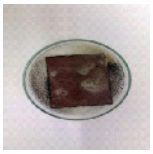
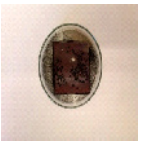
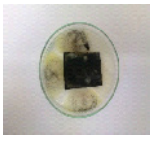
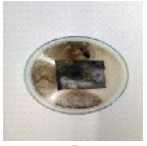
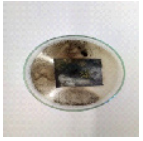
M1				
	3	3	5	5
M2				
	3	4	5	5

Mold development on leather specimens, and macroscopic images of samples treated with AF-C-1 and AF-C-2 after 7, 14, 21 and 28 days from treatment, are presented in table 3. The numbers under the images are the marks given according to the standard.

The most resistant to mold are leather samples (film-coated and uncoated brown Box leathers) treated with 80% mixture of the two antifungal products (AF-C-1, AF-C-2) in equal proportions; the samples do not develop fungi for 28 days (mark 0 for sample AF 8 and mark 2 for samples AF 7 and AF 9).

The leather samples AF 5- AF 6 (film-coated and uncoated brown and black Box leathers) treated with AF-C-2 with Roda pur 5011 containing 75% AF-C-2, as such received marks ranging between 2 and 4 after 7 days and marks 5 after 7 days.

Product AF-C-2 is less efficient, and leather samples (film-coated and uncoated brown and black Box leathers) treated with the product AF-C-2 as such received marks ranging between 3 (AF 1, AF 4) and 5 (AF 2, AF 3) after 28 days.

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Using the product as such, mattifies the film and reduces resistance to abrasion.

CONCLUSIONS

▪ The prepared antifungal and antibacterial products made of natural components (beeswax, lanolin, cedar and coriander essential oil) improve resistance of finished leather to biological factors (fungi) and can complement the treatment with biocides used for natural leather, which are toxic for humans and the environment), within the wet processing operations.

▪ Product made of cedar essential oil is less efficient, and leather samples treated with the product AF-C-2 as such received marks ranging between 3 and 5 after 28 days.

▪ The most resistant to mold are leather samples treated with 80% mixture of the two antifungal products in equal proportions; the samples do not develop fungi for 28 days (mark 0) and mark 2.

▪ Products, compatible with the materials used in the final dressing, can be used in surface treatment of finished leather and leather products in the final dressing composition.

▪ This products can be used as such in surface finishing of buffed bovine hides such as suede, buffo or nubuck to obtain a fatty/waxy feel and a better resistance to fungi of the dermal substrate.

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