FINISHING PRODUCT FOR IMPROVING ANTIFUNGAL PROPERTIES OF LEATHER

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ABSTRACT. Some biocides used in the leather industry have a certain toxicity and are prohibited by the directives in force. A product with antifungal properties containing coriander essential oil was tested as finishing auxiliary for bovine shoe upper leather. The paper presents the results obtained in leather finishing using the new product AF-C and evaluation of its antifungal activity against Aspergillus niger strain. For maximum efficiency, the concentration of AF-C antifungal product must not decrease below 65% in the final dressing for leather finishing.

KEY WORDS: leather, finishing, coriander essential oil, antifungal product

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INTRODUCTION

Biological factors (fungi, bacteria) may damage leather and leather items by degradation of the grain (stains, matting, etc.). The cost of raw materials for leather production is significant. So, the preservation of stock is still fundamental to good quality control and making a living for tanners. Yet biocides by their very nature are environmentally unfriendly. However, help may be at hand, with research into new ecofriendly brands of bacterial control [1].

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, i.e. pentachlorophenol, polyhalogenated phenolic compounds [2-5].

Many studies were aimed at replacing potentially hazardous substances used in the processing of hides, skins and furs:
- Synthesis of new classes of biocides based on derivatives of 2-amino-benzothiazole-6-substituted with methyl, methoxy, chloro, nitro, modified chemically by sulphonation [6] and used in cattle leather processing [7] which have shown to be effective against Aspergillus niger species, but not against the Trichoderma viride species;
- Synthesis of new classes of tanning agents to replace chromium in tanning hides and furs [8-15].

Several studies have been conducted on the use of natural products derived from plants for the treatment of leather and fur:
- Bayramoglu et al. [16, 17] from Ege University in Turkey used Origanum species to extract essential oils from plants through steam distillation process. It has been found that utilization of the essential
oil of *Origanum minutiflorum* during pickling has antifungal activity and that its effect is improved with increasing concentration. As a result of this study, it was found that the wet blue leather specimens treated with 1% *Origanum* sp. essential oil showed antibacterial effect on Gram-positive bacteria. *Origanum minutiflorum* essential oil had an antifungal effect on wet blue. The bacteria are more resistant to the essential oils than yeasts and moulds. A concentration of 21% relative to the float of the essential oils of oregano from three different species and fennel oil was tested for their antimicrobial activity along with 7-25% of phenol and 4-chloro-3-methyl-phenol as a commercial bactericide commonly used in the leather industry. The results showed that the three essential oils of oregano had a much stronger bactericidal activity than the commercial product and may find use as antibacterial agents in the leather industry.

- Use of essential oils in finishing leather and fur [18-20];
- Use of essential oils to stop the growth of fungi [21].

Essential oils from aromatic and medicinal plants have been known to possess potential as natural agents for leather preservation, including antibacterial and antifungal; in fact, many essential oils have been qualified as natural biocides and offered as potential substitutes of synthetic biocides in specific steps of leather processing. Many studies revealed utilization of essential oils for leather and leather objects protection against fungi [22-32].

Coriander (*Coriandrum sativum* L.) is an annual herbaceous plant originally from the Mediterranean and Middle Eastern regions, cultivated for its culinary, aromatic and medicinal use. This plant is of economic importance since it has been used as a flavoring agent in food products, perfumes, cosmetics and drugs. This culinary and medicinal plant is widely distributed and mainly cultivated for the seeds which contain an essential oil (ranges between 0.3% and 1.1%) [33]. The essential oil and various extracts from coriander have been shown to possess antibacterial, antidiabetic, anticancerous, antimutagenic, antioxidant and free radical scavenging activities [34, 35]. In addition to its culinary value, coriander is known for its wide range of healing properties.

Coriander essential oil contains 60-70% d-linalool (or coriandrol, geraniol, cimol, pinene, terpinene, phellandrene, dipentene, petroselinic acid, etc.), 15-20% lipids, 10% starch, 4-5% mineral substances, pectins, etc. [36, 37]. Coriander essential oil has bactericidal and fungicidal properties [38-41].

Coriander seed essential oil is high in linalool. European oils show monoterpene hydrocarbon content between 16 to 30%, linalool 60 to 75%, whereas a considerable amount of other oxygenated monoterpenes is also present. The main monoterpene hydrocarbon components detected in these oils are γ-terpinene (up to 10%), and limonene, p-cymene, α-pinene up to 7% each. The most prominent non-linalool oxygenated monoterpenes reported are geranyl acetate up to levels of 5%, borneol up to 7%, camphor and geranial up to 4% each and geraniol up to 2% [42].

Linalool is a tertiary alcohol isomer of geraniol and nerol, containing an asymmetrical carbon atom; it is found in nature preponderantly in isopropylidene form; it is a component of over 200 essential oils of various origins (herbs, leaves, flowers, fruits, wood); the dextrorotatory form (+) was isolated from coriander essential oil and is found in a proportion of 60-70%.

A new leather finishing auxiliary with antifungal properties (AF-C) was prepared based on beeswax, lanolin, ethanol and lauryl alcohol ethoxylated with 7 moles of ethylene oxide and coriander essential oil [18, 19].

The aims of this study are as follows: (i) to study utilization of the new product, AF-C, in leather finishing; (ii) to evaluate its antifungal activity.

**EXPERIMENTAL**

**Materials**

The chrome tanned bovine leathers, finished and crust for shoe upper: 1.2-1.4 mm
thickness; brown; obtained in the facilities of INCDTP – Division Leather and Footwear Research Institute Bucharest, Romania.

Auxiliary materials for leather finishing from TFL Company, Germany.

Roda Casicolor Brown R: viscous and homogenous fluid, dry substance 38%; pH (10% solution) 7; ash – 28%;

Roda wax MONO: dry substance 36.87%; pH (10% solution) 4.2; Ford cup viscosity Ф4, 12; kinematic viscosity 8.97 cSt; density 0.957 g/cm³;

Roda-cryl 87: dry substance 34.50%; pH (10% solution) 6.0; Ford cup viscosity Ф4, 14; density 1.025 g/cm³;

Roda-pure 302, polyurethane binder for ground coat: dry substance 36%; pH (10% solution) 7.5; Ford cup viscosity Ф4, 15; density 1.076 g/cm³;

Roda-pure 5011, polyurethane binder: dry substance 40%; pH (10% solution) 5.5; Ford cup viscosity Ф4 7; density 1.053 g/cm³;

Product AF-C with antifungal properties, prepared from coriander essential oil, beeswax, lanolin, ethanol and lauryl alcohol ethoxylated with 7 moles of ethylene oxide [18, 19] with the following characteristics: dry substance 12%; pH (10% solution) 4.5; density 0.820 g/cm³.

Methods

Chemical characteristics of shoe upper leather were determined according to the following standards:

• SR EN ISO 4684:2006 - Leather - Chemical tests - Determination of volatile matter;

• EN ISO 4048: 2008 - Determination of matter soluble in dichloromethane and free fatty acid content;

• SR EN ISO 5398:2008 - Leather - Determination of chromic oxide content; Part 1: Quantification by titration;

• EN ISO 4045:2008 - Determination of pH and difference figure;

• SR EN ISO 11640:2002 - Strength to dry and wet abrasion (1-5 ranking);

• SR EN ISO 5402:2012 - Resistance to repeated bending, number of flexions.

Antifungal activity against *Aspergillus niger*: The tests were made following standard ASTM D 4576-2013, Standard Test Method for Mold Growth Resistance of Wet Blue.

Petri dishes were placed in thermo-hygrostat at 30°C temperature and were observed and evaluated after 3, 7, 14, 21 and 28 days.

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.

Obtaining Bovine Shoe Upper Leather

Two series of experiments were performed in order to obtain cattle shoe upper leather using finishing auxiliary with antifungal properties (AF-C):

• Series I prepared with technology presented in Table 1 and with different quantities of product AF-C according to Table 2: Samples AF-1; AF-2; AF-3; control sample - M1;

<table>
<thead>
<tr>
<th>Operation</th>
<th>Composition of dispersion/Method of application</th>
</tr>
</thead>
</table>
| Basecoat (Applying Dispersion I) | 60-80 g/L Roda Casicolor Brown  
  20 g/L Roda wax MONO  
  125 g/L Roda-cryl 87  
  125 g/L Roda-pure 302  
  650-670 g/L water  
  Application by spraying 2 times |
| Intermediate pressing         | Hydraulic press using mirror or steam plate, parameters:  
  - temperature – 50-60°C  
  - pressure – 50-100 bar |
| Applying Dispersion I         | By spraying 2-3 times                                                                                       |
| Antifungal treatment / fixing  | Applying Dispersion II (see Table 2)  
  Spraying 2 times          |
| Final pressing                | Hydraulic press using mirror plate, parameters:  
  - temperature – 70-80°C  
  - pressure – 50-100 bar |
Table 2: Composition of dispersion II

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Composition of dispersion II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>AF-1</td>
<td>1000 g/L product AF-C</td>
</tr>
<tr>
<td>2</td>
<td>AF-2</td>
<td>750 g/L product AF-C, 250 g/L RODA pur 5011</td>
</tr>
<tr>
<td>3</td>
<td>AF-3</td>
<td>650 g/L product AF-C, 350 g/L RODA pur 5011</td>
</tr>
<tr>
<td>4</td>
<td>M1 Control</td>
<td>700 g/L Roda pur 5011, 300 g/L water</td>
</tr>
<tr>
<td>5</td>
<td>AF-4</td>
<td>1000 g/L product AF-C</td>
</tr>
<tr>
<td>6</td>
<td>M2 Control</td>
<td>Not finished</td>
</tr>
</tbody>
</table>

- Series II in which only finishing auxiliary with antifungal properties AF-C was used for leather finishing according to Table 2: Samples AF-4; unfinished leather was used for control sample M2. Product AF-C was compatible with the materials used in the final dressing. Leather from Experiment AF-1 was sticky after pressing. AF-C product 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.

RESULTS AND DISCUSSION

Characterization of Leather Finishing

Chemical characteristics of the leathers were determined in accordance with standard STAS 1619:1994: Leather for uppers and leather goods. Cattle skins tanned with chrome, grain finished. General technical conditions (Table 3).

Chemical and physical-mechanical characteristics of leather were within the limits specified in standard 1619:1994.

Evaluation of Antifungal Effect of Leather Finished with AF-C Product

The experiment examines how the growth of mold is influenced by existing treatment on the leather sample treated with biocides through mold resistance under simulated contamination.

Leather untreated with the AF-C product was used as a control: M1 – finished leather and M2 – not finished (crust) leather. Incubation duration was 28 days and fungal observations were performed at intervals of 7, 14, 21 and 28 days. Mold development on leather samples was evaluated by ranking according to the notation used in the standard method used: mark 0 indicates the absence of stems and a strong fungitoxic effect, and mark 5 indicates no fungitoxic effect, the mold covering the entire surface of the specimen.

Development of the Aspergillus niger strain on leather samples over time, i.e. macroscopic images of the samples are shown in Table 4.

Table 3: Chemical characteristics of bovine shoe upper leather

<table>
<thead>
<tr>
<th>Sample/Characteristic</th>
<th>AF-1</th>
<th>AF-2</th>
<th>AF-3</th>
<th>M 1</th>
<th>AF-4</th>
<th>M 2</th>
<th>STAS 1619:1994</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractibles, %</td>
<td>7.88</td>
<td>7.67</td>
<td>7.57</td>
<td>7.44</td>
<td>7.87</td>
<td>7.96</td>
<td>Max. 8</td>
</tr>
<tr>
<td>The content of chromium oxide, %</td>
<td>5.93</td>
<td>5.74</td>
<td>5.66</td>
<td>5.47</td>
<td>5.77</td>
<td>6.10</td>
<td>Min. 3.5</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry and wet abrasion strength, rank</td>
<td>5/4</td>
<td>5/4</td>
<td>5/4</td>
<td>5/5</td>
<td>5/4</td>
<td>5/4</td>
<td></td>
</tr>
<tr>
<td>Resistance to repeated bending, number of flexions</td>
<td>250.000</td>
<td>250.000</td>
<td>250.000</td>
<td>250.000</td>
<td>250.000</td>
<td>250.000</td>
<td></td>
</tr>
</tbody>
</table>
Table 4: Images of leather samples within Series I experiment

<table>
<thead>
<tr>
<th>Sample</th>
<th>7 days</th>
<th>14 days</th>
<th>21 days</th>
<th>28 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>mark</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AF-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>mark</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AF-3</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>mark</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Control M 1</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 5: Images of leather samples within Series II experiment

<table>
<thead>
<tr>
<th>Sample</th>
<th>7 days</th>
<th>14 days</th>
<th>21 days</th>
<th>28 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF-4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>mark</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control M 2</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>mark</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

In the two series of experiments, the leather samples AF-1 and AF-4 were the most resistant to mold, the samples did not develop fungi for 28 days - mark 0; the leather sample AF2 did not develop fungi for 21 days - mark 0; the leather sample AF3 developed fungi after 7 days - mark 2. It can be observed that the fungitoxic effect decreased with reduced quantities of AF-C used in the final dressing composition.

The negative control leather M1 and M2 (without product AF-C) already failed in the first week and received marks ranging between 4 after 7 days and 5 after 14 days.

Moisture content and pH of the leather have been reported as the main biotic factors affecting the fungal deterioration. In the present investigation, the volatile matter content and pH of leather ranged between 13.78 and 14.76%, and between 4.5 and 6, respectively. So, the fungal distribution on the samples was not influenced by their moisture content and pH.

The finishing auxiliary with antifungal
properties AF-C improved resistance of finished leather to biological factors (fungi). For maximum efficiency, the concentration of the antifungal product must not decrease below 65%.

CONCLUSIONS

Results showed that the AF-C product containing coriander essential oil could be used as natural antifungal in leather finishing. The AF-C product can be used in surface treatment of bovine finished leather for shoe upper and 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. The AF-C product improved resistance of finished leather to biological factors (fungi) and can complement treatment with biocides used to treat natural leather in wet processing operations. For maximum efficiency, the concentration of the antifungal product must not decrease below 65% in the final dressing for leather finishing.

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REFERENCES


