NEW PRODUCTS BASED ON ESSENTIAL OILS FOR FINISHING NATURAL LEATHERS WITH ANTIFUNGAL PERFORMANCES – PART 1

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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. Products with antifungal and antibacterial properties were obtained, containing cedar essential oil, emulsion of beeswax and lanolin mixture in a 1/3 ratio, stabilized with ethoxylated lauryl alcohol and ethyl alcohol. This paper presents the process of obtaining and characterization, by physico-chemical and spectral analyses, of new product based on cedar essential oil, ethyl alcohol, non-ionogenic surfactants from the category of polyethoxylated fatty alcohols and wax emulsions containing beeswax, lanolin and non-ionogenic emulsifier. Cedar essential oil contains: thujopsene – 37.25% and cuparene – 9.47% with antibacterial and antifungal properties, cedrenol – 20.79% and cedrene – 20.03% with antimicrobial properties as main components. The spectrum of the product based on cedar essential oil, contains all the bands of components: an intense band at about 2925 cm⁻¹ and weaker one at about 2874 cm⁻¹ assigned to asymmetrical and symmetrical stretching vibrations of methyl and methylene groups of cedar oil, beeswax and lanolin; a weak band around 1643 cm⁻¹ due to the stretching of the C = O bond of ester groups, two more intense bands at 1455 and 1374 cm⁻¹ specific to compounds containing long aliphatic chains, and bands at about 1087 and 1045 cm⁻¹ assigned to C-O-C bonds of ether. The prepared product are yellowish white fluids, homogenous, with 11-18% dry substance, pH – 3.8-4.5, density – 0.805-0.820 g/cm³.

Keywords: essential oils, FT-IR spectrometry, Gas Chromatography Mass Spectrometry (GC/MS)

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 Pharmacopoeia, 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

Cedar essential oil (Solaris Plant, Bucharest), containing 37.25% thujopsene, 20.03% cedrene, 20.79% cedrenol, cuparene etc.

Beeswax (Happynatura, Bucharest), solid with specific odour, yellow colour, melting point 62-65°C.

Lanolin (Medchim, Bucharest), solid greasy compound with specific odour, light yellow colour, melting point 38-42°C.

Nonionic emulsifier – lauryl alcohol ethoxylated with 7 moles of ethylene oxide (Elton, Bucharest), melting point -15°C, ignition point over 170°C, density – 0.97 g/cm³ at 40°C, pH – 5-7, viscosity – 25 mPa x s.

Ethanol (Chemical Company, Germany), density – 0.789 g/cm³ at 20°C, boiling point – 78°C, melting point –114°C, water solubility – in any proportion.

Methods

The product with antifungal properties was prepared in an equipment consisting of a reaction vessel with 3L capacity and a heating system (electric bath with temperature control). The 3-necked reaction vessel, made of high-temperature resistant glass, is equipped with a propeller stirrer to homogenize the reaction mass, a thermometer for temperature control and condenser connected to the water source to maintain the temperature constant during the preparation process.

Gas Chromatography Mass Spectrometry (GC/MS) Analysis: Analysis of the essential oils carried out by using Agilent 7890 A GC System equipped with Agilent 5795 C MS, and HP-5 MS (0.25 mm x 30 m i.d., film thickness 0.25). The carried gas helium (99.9%) at a flow rate of 1 mL/ min; ionization energy was 70 eV. Mass range m/z 50-650 amu. Data acquisition was scan mode. MS transfer line temperature was 250 °C, MS Ionization source temperature was 230 °C, the injection port temperature was 250 °C. The samples were injected with 250 split ratio. The injection volume was 1 µL. Oven temperature was programmed in the range of 50 to 250 °C at 3°C/ min. The structure of each compound was identified by comparison with their mass spectrum (Nist 05 and Wiley 7 library).

Attenuated Total Reflectance Fourier transform infrared spectroscopy (ATR-FTIR) measurements were run with a Jasco instrument (model 4200), in the following conditions: wavenumber range – 4000-600 cm⁻¹; data pitch – 0.964233 cm⁻¹; data points – 3610; aperture setting – 7.1 mm; scanning speed – 2 mm/s; number of scans – 30; resolution – 4 cm⁻¹; filter – 30 kHz; angle of incident radiation – 45°.

Components Used to Obtain Antifungal and Antibacterial Products

The chromatogram of cedar oil is shown in figure 1, and identification of compounds in their composition is presented in table 1.

Figure 1. Chromatogram of cedar oil

Table 1. Identification of organic compounds in the cedar essential oil by GC-MS

RT	Amount, %	Compounds
35.19	0.87	α -Humulen
36.13	0.57	trans-Cariofilen
36.74	20.03	Cedrene
37.11	4.58	α -Funebren
37.56	37.25	Tuiopsen
38.62	0.50	Aromadendrene
39.08	1.08	ar-Cucumen
40.65	9.47	Cuparen
40.92	1.10	Z,E α -Farnesen
41.61	1.63	α -Longipinen
44.46	0.51	Epiglobulol
45.01	20.79	Cedrenol
45.69	0.87	cis-Farnesol
47.38	0.74	α -Bisabolol

Cedar essential oil contains: thujopsene – 37.25% and cuparene – 9.47% with antibacterial and antifungal properties, cedrenol – 20.79% and cedrene – 20.03% with antimicrobial properties as main components.

Obtaining Antifungal and Antibacterial Products

The antifungal product based on cedar essential oil (marked AF-C-2) was obtained from 80 % cedar essential oil, 10 % wax emulsion, 5-10 % ethanol and 5-10% ethoxylated lauryl alcohol.

The wax emulsion was obtained from: 15-20% wax mixture 1/3, 10% ethoxylated lauryl alcohol reported to the amount of wax emulsified and water under stirring (300-500 rot/min), at 60-80⁰C.

The wax mixture was obtained by beeswax and lanolin (1:3) liquefied by heating at 80-90⁰C and stirring for 40-60 min (60-80 rot/min).

RESULTS AND DISCUSSION

Physical-Chemical Characteristics of Antifungal Product Based on Natural Oils and Waxes

The prepared product AF-C-2, are yellowish white fluids, homogenous, with 11-18% dry substance, pH – 3.8-4.5, density – 0.805-0.820 g/cm³.

FT-IR Characterization of Components Used and Produced with Antifungal Properties Obtained

FT-IR spectra of the components of the antifungal products AF-C-2, containing cedar oil, beeswax and lanolin and of the films obtained thereof by evaporation are presented in figure 2.

Figure 2. Overlapping FT-IR spectra of cedar oil, waxes and film obtained from the antifungal and antibacterial product AF-C-2

The spectrum of the AF-C-2 contains all the bands of components: an intense band at about 2925 cm⁻¹ and weaker one at about 2874 cm⁻¹ assigned to asymmetrical and symmetrical stretching vibrations of methyl and methylene groups of cedar oil, beeswax and lanolin; a weak band around 1643 cm⁻¹ due to the stretching of the C = O bond of ester groups, two more intense bands at 1455 and 1374 cm⁻¹ specific to compounds containing long aliphatic chains, and bands at about 1087 and 1045 cm⁻¹ assigned to C-O-C bonds of ether.

CONCLUSIONS

- Cedar essential oil contains: thujopsene – 37.25% and cuparene – 9.47% with antibacterial and antifungal properties, cedrenol – 20.79% and cedrene – 20.03% with antimicrobial properties as main components.
- The spectrum of the AF-C-2 contains all the bands of components.
- The prepared product AF-C-2, are yellowish white fluids, homogenous, with 11-18% dry substance, pH – 3.8-4.5, density – 0.805-0.820 g/cm³.

▪ The prepared antifungal and antibacterial product made of natural components (beeswax, lanolin, cedar essential oil) will be tested to determine the resistance to fungi of the natural leathers treated with this product.

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REFERENCES

- Bayramoglu, E.E. (2007), "Unique biocide for the leather industry: essential oil of oregano, *JALCA*, 102(11), 347.
- Cadirci, B. *et al.* (2010), "Physical and antimicrobial characteristics of aloe vera treated split suede leather", *JALCA*, 105(2), 34.
- Chirita, Gh. and Chirita, M. (1999), *Tratat de chimia și tehnologia pieilor și blănurilor*, vol. I, Ed. Gh. Asachi, Iași.
- Council of Europe (2005), *European Pharmacopeia*, vol. II, ESCOP Strasbourg.
- David, V. and Medvedovici, A. (2008), *Methods of separation and chromatographic analysis*, University of Bucharest Press.
- Heidemann, E. (1994), *Fundamentals of Leather Manufacturing*, Eduard Roether KG Druckerei und Verlag, Darmstadt.
- Moldovan, Z. (2001), *Instrumental Analysis Methods*, University of Bucharest Press.
- Niculescu, O. and Manta, A. (2013), "Products with antifungal properties for finishing natural leather and leather items", Patent Application OSIM A/00538.
- Niculescu, O. *et al.* (2015), "Obtaining and characterizing a product with antifungal properties based on essential oils and natural waxes for finishing natural leathers", *Rev. Chim. (Bucharest)*, 66(11), 1733-1736.
- Niculescu, O. *et al.* (2017), "Finishing product for improving antifungal properties of leather", *Leather and Footwear Journal*, 1, 31-38, <https://doi.org/10.24264/lfj.17.1.4>.
- Sirvaityte, J., Siugzdaitė, J. and Valeika, V. (2011), "Application of commercial essential oils of Eucalyptus and Lavender as natural preservative for leather tanning industry", *Rev. Chim. (Bucharest)*, 62(9), 884.
- *** (1998), *Romanian Pharmacopoeia*, 10th edition, Medical Ed., Bucharest.
- ***, Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control).
- ***, ST 12697/A 91/2008, Standard for Determination of Leather Resistance to Fungi.