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Research on application of flax and soya oil for leather fatliquoring

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ABSTRACT

The aim of this research was the application of compounds based on vegetable oils, not chemically modified, for leather fatliquoring.

Emulsions were obtained by using mechanical mixing natural oils with emulsifiers. Oils were not chemically modified. Oils used in the study contain large amounts of double bonds which should provide a good binding to the fat in the leather.

Properties of the obtained emulsions were defined, as well as those of fatliquored leather. Researches showed that the way in which emulsions are prepared influences their stability. It was also stated that properties of fatliquored leather (crust) with researched emulsions are similar to properties of crust treated with commercial products, among others, chemically modified natural fats. It seems that with fats with high iodine value, the softness of the leather is similar. Despite the fact, that unbound fat content in leather fatliquored with commercial products was higher than in leather fatliquored with vegetable fats with high iodine value.

1. Introduction

Leather production technology consists of many phases which can be divided into processes of chemical and mechanical treatment. During the chemical treatment, among others, hides structure loosening takes place, as well as the removal of undesirable components including natural fat. The removal of fat causes collagen fibers to stick together and then the leather becomes stiff. In order to prevent that leather is fatliquored after the tanning process. Fat molecules introduced into the leather in fatliquoring process isolate collagen fibers; as a result, leather becomes soft, malleable and suitably elastic. As a result of chemical modification of natural fats the wastewater and solid waste is created (www.echa.europa.eu).

Production of such fats normally causes negative influence on the environment. Therefore, ideas of fat applications for leather without their chemical modifications seems to be a “clean” technology for the environment.

Fatliquoring is one of the final operations of wet finishing process. It consists in introducing, mainly in water environment, into the wet leather of determined quantity of fatliquoring and lubricant agents that soften and plasticize its fibrous structure. Fatliquoring has a strong effect on leather mechanical properties and physical features. After tanning the leather is hard, stiff and more or less prone to fractures in its grain side. Therefore, independently from the tanning method, it requires specified fatliquoring. After drying, fibers of wet fatliquored leather (crust) do not paste one to another and can be isolated from each other by mechanical treatment of dry leather, thanks to what we obtain natural leather grip (Lasek, 1984).

For fatliquoring, most commonly used are natural animal or vegetable fats after chemical modification in form of water emulsions. In practice, to fatliquoring of leather are usually used natural fats with iodine value, about 80 g iodine/100 g oil (e.g. castor oil). In these studies was used vegetable oil with much higher iodine value: flax oil (iodine value: min. 175 g iodine/100 g oil) and soya oil (iodine value: min. 125 g iodine/100 g oil). Oils used in the study contain large amounts of double bonds which should provide a good binding to the fat in the leather.

Depending on presence of different additives, emulsions can be more or less stable (Lasek, 1978). Leather as absorbent has a decomposing influence on the emulsion. Fat emulsion should be stable; so that it does not decompose instantly after the contact with leather; at the same time it cannot be too stable, because it will not possess adequate fatliquoring properties.

1.1. Emulsifiers in leather tanning

Emulsifiers are surfactants that have the ability of significant lowering the water surface tension. Emulsifiers can be divided into four groups:

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- anionic, where active group is negatively charged;
- cationic, having positive charge groups;
- amphoteric, which have charges of both kinds (their charge depends on pH of the environment);
- non-ionic, non-dissociation, containing hydroxyl or ethoxy groups (Bieńkiewicz, 1986).

They are used in almost all chemical processes of leather tanning. They find a wide application, among others, in processes of beamhouse, pickling, tanning, as well as dyeing and especially in fatliquoring, where those agents play an especially important role. They are also used for impregnation and the leather finishing where they are bounded and retained in the leather (Maldonado et al., 1988). Emulsifiers influence dispersion properties of fatliquor agents, their resistance to temperature, pH changes and neutral electrolytes, as well as number of their technological properties (Friese, 1988). Thanks to those properties the important role is played by penetration into the porous structure of leather (Langmaier, 1991).

1.2. Production of fatliquor agents

For the production of fatliquor agents, natural oils, as well as animal and vegetable fats, are most frequently used (Santos and Gutterres, 2007). There are also ways to use the fat of seal skins for the production of fatliquor agents (Cuq et al., 1998).

Natural fats in its original form are very rarely used for leather fatliquoring. That is why, before their application in fatliquoring process they are modified to obtain solubility or emulsion in water is made from them. Solubility is obtained by chemical modification of natural products (sulfation, sulfonation) with use of sulfuric acid, monohydrate or oleum (Michalec, 1991). Another modifying factor may be oxyethylated ethylene oxide gas. Obtained in this way fatliquoring agent based on sunflower oil used has a high HLB values, high stability of water emulsion as well as high stability against acids, alkalies and different metallic salts. Leather fatliquored with this agent shows good properties (EL-Shahat et al., 2011).

There is also a possibility of creating fatliquoring emulsions through emulsification of natural fats with emulsifies using different kinds of mixing, for example by ultrasounds (Sivakumar et al., 2008a). Ultrasounds have also been used as a tool for preparation of fatliquor emulsion using tallow fat, eliminating the conventional sulfation process with judicial use of emulsifying agents. The applicability has been examined by utilizing the emulsified fat in leather fatliquoring process. Fat content in leather has been analyzed and the results show emulsions prepared using anionic emulsifier yielded better fat uptake in leather (Sivakumar et al., 2012).

Ultrasounds have also been used both in fatliquoring of leather (Sivakumar et al., 2009a), and other tanning processes (Sivakumar et al., 2007). Ultrasound is also used to degreasing wool (Bahtiyari and Duran, 2013). Dyeing in the presence of ultrasound increases the dye exhaustion and reduces dyeing time compared with the process in the absence of ultrasound under stationary conditions (Sivakumar and Rao, 2001). The studies of the use of ultrasound in improving the diffusion process through porous skin/leather matrix (Sivakumar et al., 2008b). The use of ultrasound also increases efficiency and facilitates the degreasing of sheepskin (Sivakumar et al., 2009b).

For leather fatliquoring we apply, above all, emulsions of oil in water type. Regardless of the production method, in order to be able to apply emulsion for leather fatliquoring it has to possess adequate stability, because only stable emulsions ensure desirable fatliquoring effects and require leather properties.

The basic analysis of fatliquored leather is determining the content of fat in leather by the Soxhlet extraction method. Research the effects of fatliquoring of leather can be performed using an acoustic test (Liu and Latona, 2002). The quality of fatliquoring agents applied to leather can be assessed on the basis of DSC (Manich et al., 2005).

From a technical point of view, a better way to produce fatliquor emulsion based on vegetable oils with high iodine value and emulsifiers can be the use of mechanical effects (intensive mixing). Furthermore, the use of vegetable oils with a high amount of double bonds should give good binding to the fat from leather. Therefore, it is interesting to examine the effects of fatliquoring using fatliquor emulsion, prepared from vegetable oils with high iodine value, and emulsifiers. High iodine value has also fish oils. However, fatliquor agents based on fish oils give leather unpleasant smell.

Furthermore, trends in the world production of vegetable and fish justifies the themes presented in the work. In the last 40 years, the production of soya oil increased seven times (Carlsson, 2009). Also, the world soybean stocks are still growing. The stocks of soybean were 55 million tonnes on the beginning of the year 2012, however these stocks increased to 60 million tonnes on the beginning of the year 2013 (www.usda.gov/oce/commodity/wasde). Simultaneously there has been a slight decrease in catching marine fish in the years 2003–2009 at about 25% (www.faostat.fao.org/site/368/default.aspx#ancor). Raw oil which is the basis for the production of vegetable oils belong to the renewable raw materials. The increase in production of vegetable oils is beneficial for the environment. The increase of the oil plantations conducive to reduction of carbon dioxide in the air. However, fish oil sourcing is limited. Trends in environmental protection lead to a reduction of catching marine fish, and this is not conducive to the growth of obtaining fish oil.

2. Experimental section

2.1. Experimental set-up

The first research phase consisted of emulsions production, based on vegetable oils: flax and soya, as well as determining their properties. Non-ionic surfactants were applied as emulsifiers. The next phase was the introduction of obtained emulsions to wet-blue leather. Then was analyzed of properties of the crust leather.

2.2. Materials and methods

In order to obtain fatliquor compounds there were used flax oil and soya oil, as well as non-ionic surfactants. Flax oil and soya oil – edible, refined vegetable oils used for food purposes.

Characteristics of applied materials were detailed below

Flax oil – TYPE J1 ROL (distribution P.P.H.U Eliot)

1. Iodine value:	min. 175 g iodine/100 g oil
2. Density in temp. 20 °C:	±0.930
3. Water content:	max. 0.1%
4. Fatty acids composition:	$C_{16}:0$ 5 – 7%
	$C_{18}:0$ 2.5 – 5%
	$C_{18}:1$ 16 – 24%
	$C_{18}:2$ 12 – 18%
	$C_{18}:3$ 50 – 60%