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Research of the Effect of Esters Used in Fatliquoring Leather for Shoe Uppers

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Annotation: This work is a research by the method of IR spectroscopy of the fatliquoring process based on a new fatliquoring agent-ester, absorbed by the leather, and its physical and mechanical characteristics. As a result of research, it was found that when an ester interacts with functional groups of collagens, hydrogen bonds are mainly formed. As a result, it is partially deposited between the fibers, and also combines with the leather substance. In this case, the surface of the fibers is enveloped in a film of fat, which separates them and thereby prevents adhesion during evaporation of water during the drying process of the leather. Researches have established that the use of an ester is possible as a fatty component for the production of natural leather, which leads to a deeper and more even distribution of fat in the dermis.

Key words: ester, fusel oil, crude fatty acids, collagen, performance properties, fatliquoring process, fat distribution.

Fatliquoring in the tanning industry provides for the processing of semi-finished leather products, the principle of which is to introduce softening and fatty substances into the wet semi-finished product. Based on their intended purpose of the finished product, as a result of fatliquoring, the basic properties of the leather, such as softness, elasticity, plasticity and hydrophobicity, change.

The high demands made recently to the consumer properties of natural leather and the general shortage of fatty materials were the basis for the development of new preparations with multifunctional properties.

Obtaining leather with the necessary performance properties is largely ensured by the choice of fatliquoring materials, the conditions for the fatliquoring process. Therefore, it is always topical to study new materials with a view to their further use in the leather industry.

Developed and passed extensive industrial tests [1], fatliquoring preparations of the CMX series, based on new synthetic products - emulsifiers, such as sodium salts of alkyl sulfosuccinic acid, alkyl phosphates. CMX-470 is a stable synthetic fat electrolyte based on sodium salts of alkylsulfosuccinic acid and synthetic fats. The leathers treated with this fat are soft, have a low specific gravity, are pleasant, not dry, have light and heat resistance. The fatty preparation has been tested and successfully used for lining and haberdashery leathers, for leathers with varnish coating.

Research was conducted [2] to investigate the effect of the type and dosage of fat on the physical properties of tuna uppers. The types of fats used are natural and synthetic, and their dosages are 3%, 6%, 9%, 12% and 15%. The increase in thickness, tensile strength, elongation at break and organoleptic properties of the leather are investigated. The best results in this study are synthetic fat at a dosage of 3%, which was obtained from leather with a 32.4% increase in thickness, tensile strength 95.3 N/mm, tensile strength 27.9 N/mm^2, elongation at break 45.3%, dark brown, smooth to the touch, had good flexibility.

In the modern method of fatliquoring the skin, emulsions of oils in water (fats), prepared with the use of emulsifiers, are used. More precisely, the fatliquoring process is the sum of three processes: wetting the surface, applying an oil emulsion, and applying oil to the fiber bundles. This method has disadvantages due to the high-water consumption for oil diffusion and discharge of emulsifiers carrying waste water. The work [3] describes a new approach to the preparation of fatliquoring compositions based on solvent oil that do not contain emulsifiers to obtain the necessary softness of the leather.

The distribution of fatty materials over the thickness of the leather is of great importance, since the more of them in the middle layer, the softer the leather. Penetration depth is a function of the stability of the fat emulsion: the lower the surface tension, the easier the particles penetrate into the leather. However, the depth of penetration of fat is influenced not only by surface tension, but also by its viscosity. The lower the viscosity, the faster and deeper the fat penetrates. Penetration can be increased by adding to the composition an ester obtained on the basis of secondary and by-products of the oil and fat and hydrolysis industries [4].

The nature of the interaction of the fatty material with the leather depends on its structure, and on the structure of the fatty substance. The nature of this interaction can be judged by the change in the infrared spectrum of the protein. IR spectra, being absorption spectra of electromagnetic radiation, are associated with a change in the dipole moment of the molecule. Since IR spectroscopy is based on periodic changes in the position of atoms in a molecule without shifting its center of mass, these motions are called normal vibrations. Vibrational spectroscopy methods are also successfully used to solve problems of structural research, namely, to study the nature of chemical bonds, determine the geometry of a molecule, and to study intra- and intermolecular interactions in the systems under study.

In this direction, studies were carried out on fatliquoring of chrome leather for shoe uppers with ester in comparison with fatliquoring with natural fat and non-greasy leather.

In this work, for research, we used fatty substances for the skin containing esters obtained by us from by-products and secondary products of local production [5] and a traditionally used natural imported fish oil product.

The research was carried out in the laboratory "Center for Advanced Technologies" of the Ministry of Innovative Development of the Republic of Uzbekistan using the Nicolet iS50 FT-IR spectrometer according to the method [6].

Results

Comparison of the IR-spectra of non-fatty leather and leather, fattened with various fatty substances, showed that depending on the type of fat-fatty substance changes and the IR spectrum of fatty leather. Small changes in the structure of leather are observed in the case of leather treatment with an ester (Fig. 2). For comparison, the IR spectrum for non-aged leather is shown (Fig. 1).

A peak appears in the spectrograms (Fig. 1) in the region of 3295.86 cm^{-1}. Stretching vibrations, one of the most characteristic for the IR spectrum, forms an intense band in the region of 3200-3600 cm^{-1}. The position and character of the band depends on the degree of participation of the hydroxyl group in the hydrogen bond.

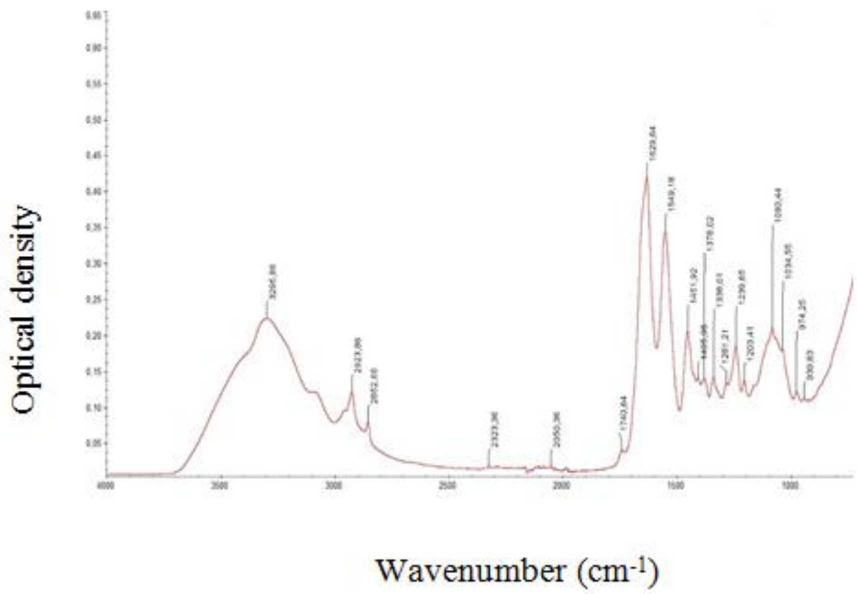

Figure 1 IR spectrum of non-aged leather

Stretching vibrations of NH appear in the region of 3500-3100 cm^{-1}, the intensity of the bands in the IR spectrum is much lower than that of the OH bands in the same region. Secondary amines give only one lane. When a hydrogen bond is formed, the vibration frequency decreases and the bands broaden. Sometimes free and hydrogen-bonded forms are observed simultaneously. In addition, a broad, highly structured band in the range of 3000-2000 cm^{-1} is manifested by amines (NH_3 +, NH_2 +, NH +) of average intensity in the stretching vibration [7].

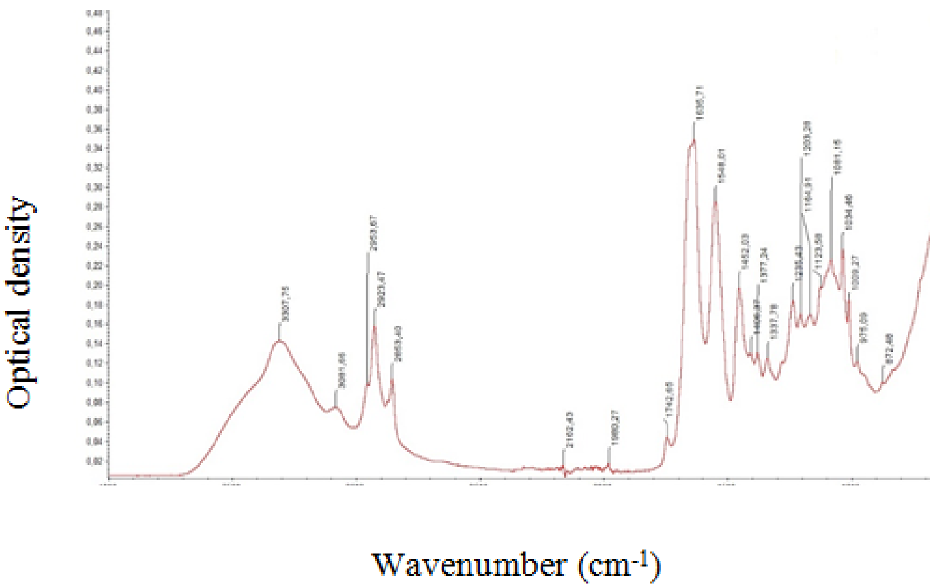

Figure-2 IR spectrum of fatty leather with fish oil

An analysis of the data obtained showed that in the spectrum of leather fattened with fish oil (Fig. 2), the absorption band at 3295.86 cm^{-1} in non-skinned leather (Fig. 1), which characterizes the vibration frequency of the OH-groups of collagen, appears in the band at 3307.75 cm^{-1}, and the bands at 2953.67, 2923.47, 2853.40, and 2162.43 cm^{-1}, which also characterizes the vibration frequency of the NH-groups of collagen, is shifted to the vibration region of 3081.66 cm^{-1}.

Similar changes are observed in the spectra obtained for leather, fattened with ester (Fig. 3). The OH group appears at the 3300.81 cm^{-1} band, and the band that also characterizes the vibrational frequency of the NH groups at 2956.05, 2924.31, 2871.85, 2853.80, 2323.27, 2161.86, and 2050.07 cm^{-1} is shifted to the vibrational region of 3080.69 cm^{-1}.

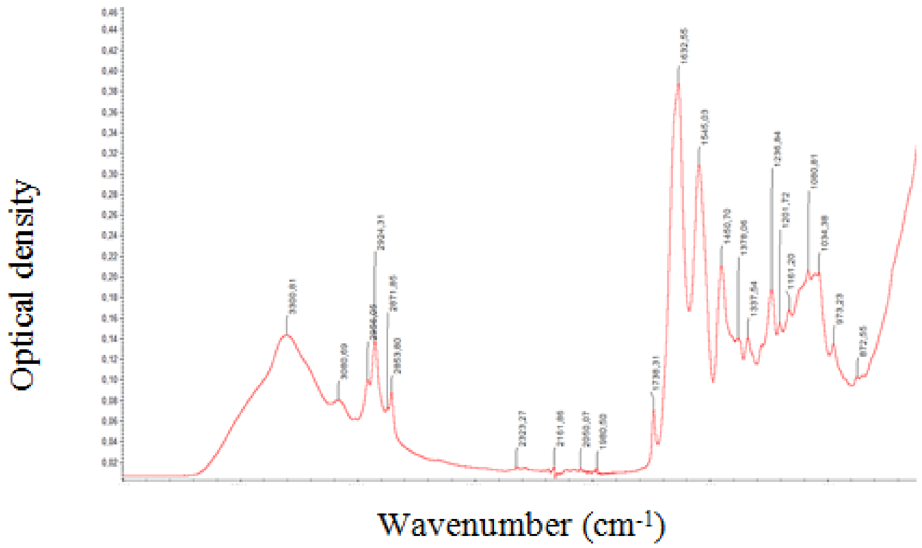

Figure-3 IR spectrum of fatty leather with ester

Based on these data, it can be assumed that hydrogen bonds are formed between the oxygen-containing fat groups and the NH-groups of collagens in both samples; however, the absorption band of fish oil is much smaller (Fig. 2) than in the case of leather fattened with ester (Fig. 3).

Discussions

Most of the very important functional groups and structural fragments detected by infrared spectroscopy have absorption bands in the range of stretching vibrations of double bonds of 1500-2000 cm^{-1}. In addition to aromatic compounds, carbonyl compounds and their nitrogenous analogs, carboxylic acids and all their derivatives, heterocycles containing C = C, C = N or N = N bonds are absorbed here. In addition, in the spectra (Figs. 2-3), a new interference of 1980 cm^{-1} appeared, which characterizes the COO groups [7], which is absent in tanned leather.

It should be noted that absorption bands characterizing these bonds appear after treatment with fatty materials. This indicates that when the leather is treated with a fatty substance, along with the formation of double bonds, it also interacts with the hydrophobic areas of collagen.

Vibrations of ester groups are manifested in the region of 1742.65 and 1635.71 cm^{-1} (Fig. 2), and the most intense in the spectra of fatty leather with ester (Fig. 3) in the regions of 1738.31 and 1632.55 cm^{-1} in which an increase in the width of the peaks is observed, which indicates a rupture of the carbon chain and an increase in free CH_3 groups in the molecule. In addition, it is known [7] aliphatic esters absorb at 1750-1735 cm^{-1}, when conjugated, this frequency decreases (α, β-unsaturated esters: 1730-1710, aromatic esters: 1730-1715). α-Halogenated derivatives absorb at 1790-1740 cm^{-1}.

Research into the use of an ester has shown the possibility of its use for fatliquoring leather. The ester has the following advantages over natural fats: it does not oxidize, has fungicidal properties and is more stable in chemical composition and physical properties.

CONCLUSIONS

Thus, on the basis of laboratory and production tests, it was established:

the use of an ester is possible as a fatty component for the production of natural leather;

the use of an ester leads to a deeper and more even distribution of fat in the dermis;

In addition, the IR spectroscopic research indicates that the composition of fatty materials is characterized by the presence of polar molecules, as a result of which they are strongly associated with the polar groups of collagen and tanning agents.

In the process of fatliquoring, an ester-based composition penetrates into empty cells of the dermis. This process changes the chemical and physical-mechanical characteristics of the leather, making it softer, more elastic, durable, flexible and gives a smooth textured surface.

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