Influence of a fluorine-containing compound on the water-repellent properties of leathers. Report 1. Study of a possibility to apply a perfluoroaromatic compound to increase water-resistant properties of the leathers

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Summary: Application of a new water-repellent compound, octafluorotoluene(C7F8), for chrome tanned upper leather treatment has been studied. A small addition of the perfluoroaromatic compound (0.25% of the leather shaved mass) in the stage of dubbing (the content of the dubbing mixture: 50% of synthetic fat, 20% of sulfonated fish oil,20% of paste *VNIIG*, 10% of spindle oil; mixture consumption is 6-8% of the leather shaved mass) results in an increase in water resistance: water permeability is reduced 6.5-33.9 times (0.77-4.03 in comparison with 0.118-0.120g/cm2 h), *water drench* under dynamic conditions changes 1.5-5.4 times (21-75 in comparison with 103-122 min).

The improvement of water-resistant properties of leathers is associated with adsorption of octafluorotoluene, hydrophobic and structure-forming effects.

Key words: *fluorine-containing compound, hydrophobicity, dubbing and dyeing leathers, water permeability, adsorption, structure-forming effect.*

Hydrophobic properties of leathers, their water resistance evaluated by *water drench* and water permeability indices and by an effect of stability to water drop at wetting etc. are important colloid-chemical and performance characteristics influencing the leather quality (wear resistance, durability).

A special treatment of leather with substances of a different chemical nature with the purpose of water repellency treatment is known to carry out together with dubbing or in the finishing stage of leather treatment [1-4]. The use of such well-known water-repelling agents [4] as chromolan (13% of the sample mass), organosilicone fluid GKG-94 (3-56% of the sample mass), a product on the basis of a mixture of synthetic and natural fats, a paraffinic emulsion (6% of the sample mass) etc., is limited because of a number of shortcomings: a reduction of hygienic properties (vapor permeability) of leathers (except a treatment with chromolan), the use of the paraffinic emulsion results in leather fatness by touch, organosilicone water repellents are not bound up with leather stably and water resistance is gone with time. Chromolan preparations are combustible in isopropyl alcohol.

Recently chlorofluoroorganic compounds are used in domestic and foreign practice of leather manufacturing. Their application has considerable advantages in comparison with conventional ones: high adsorption, strong binding with leather, incombustibility. Fluorine-containing compounds give leather not only hydrophobic, but also oleophobic properties, heat resistance etc.[1-6]

So, leather treatment with fluorinated furan derivatives[6], fluorine-containing polymers and co-polymers, for example with dihydroperfluoroheptylacrylate (latex GF) and its copolymer with N-methylmethacrylamide (latex LFM)[4] , results in the increase in water-resistant properties. But using latexes reduces vapor permeability of development samples in comparison with check reference ones, that may be associated with closed water repellency, i.e. filling intervening fibrous space of leathers with molecules of water-insoluble polymer obviously resulting in the reduction both air permeability and vapor permeability of leathers[2].

We studied the use of a perfluorinated compound, octafluorotoluene (C7F8)[7] in treatment of different types of leathers with the purpose of water-repellency treatment . The use of this substance is caused by its availability and safety in work (hardly combustible, nonexplosive liquid). Economic efficiency is attained at the expense of small additions at moderate prices. According to the experimental results, water-resistant properties of leathers after their treatment with octafluorotoluene are improved and the increase in *water drench* index and the reduction of water permeability is the evidence of that [8]. Water-repellency treatment of leathers with the use of octafluorotoluene is carried out together with their drumming in an experimental drum under half-industrial conditions according to the leather in sides method at Novosibirsk JSC “KORS”. The leathers chrome-tanned are placed in the experimental drum and treated according to the method of upper leather manufacturing. For drumming the following content of fats is used: 50% of synthetic fat, 20% of sulfonated fish oil, 20% of paste VNIIG, 10% of spindle oil; the mixture consumption is 6-8% of the leather shaved mass. Octafluorotoluene is added in an amount of 0.25% of the leather shaved mass and treatment (at 60-65 ^{O}C) is then carrying out for 1 hour at vigorous stirring. After the drumming and dyeing the leathers are finished according to the existing technology. The finished leather is subjected to topping with a dye containing acrylate copolymers.

The change in water-resistant properties of leather in sides treated with octafluorotoluene and without it was determined according to State Standard GOST 938.23-71 on a PVD-2 instrument (

Table1

I*ncrease in water-resistant properties of leathers after their treatment with octafluorotoluene*

Leather samples	Water drench under dynamic conditions, min	Water permeability, g/cm2 h
Development samples	103-122	0.118- 0.120
Check reference samples	21-75	0.77-4.03

It is seen from the table data that the water-resistant properties of the leathers are improved: the water permeability reduces 33.9 times maximum, the *water drench* changed 1.5-5.4 times.

The improvement of water-resistant properties of the leathers after subjection to octafluorotoluene is confirmed by the effect of stability against a water drop according the method of a “sitting drop” [2]. In the case of the development samples the time of absorption of the water drop is about 2 hours and it is equal to 20 minutes in the case of the check reference samples.

The water-resistant properties of leathers after treatment with octafluorotoluene can be explained by the structure- forming effect arising from C7F8 adsorption. Adsorption of octafluorotoluene may be a result of intermolecular interaction (Van-der-Waals forces, hydrogen bonds with participation of strong electronegative fluorine atom, donor-acceptor type bonds) of this compound with the leather components (collagen-protein of the leather etc.)

It is impossible to exclude formation of covalent bonds at nucleophilic substitution of fluorine atom of octafluorotoluene [9] with a remainder of protein aminoacids. In this case it would be irreversible binding octafluorotoluene with the leather. The use of a different active fluoroarene, 2,4-dinitrofluorobenzene, to determine the end nitrogen atom in peptides as a result of nucleophilic substitution of the fluorine atom with peptide aminogroup [10] is well known.

The arising water repellency of the leather surface treated with octafluorotoluene obviously reflects a well-known fact that fluorinated surfaces are not wetted with water [11,12]. In contrast to leather treatment with fluorine-containing polymers which may lead to closed water-repellent treatment, octafluorotoluene , as a low-molecular compound, can be adsorbed on the leather according to open water-repellent treatment phenomena without reducing its hygienic properties (vapor permeability).

Thus, it has been shown that a small addition of a new water-repellent compound, octafluorotoluene, in the stage of leather dubbing (drumming) results in the water resistance increase of the leathers that can be caused by octafluorotoluene adsorption, structure-forming and water-repellent effects.

References

1. Safonova Z.V., Volkov V.Z. Sovremennye metody gidrofobizatsii i napolneniya kozh. Obzor. Inform. TsNIITEIlegprom.-M: 1986.

2. Mozer E. Novye gidrofobiziruyushchie sredstva dlya povysheniya vodostojkosti kozh i mekhovogo velyura. Kozhevenno-obuvnaya promyshlennost'. 1991. № 5. s. 4-6.

3. Markaryan S.M. Simonyan S.G., Petrosyan V.A. Gidrofobizatsiya kozh ftororganicheskimi polimerami. Kozhevenno-obuvnaya promyshlennost'. 1988. № 11. s. 47-49,

4. Makarov-Zemlyanskij Ya.Ya., Fomina T.T., Dondarova T.I., Chursin V.I. Vliyaniekhimicheskoj prirody gidrofobizatora na vodostojkost' obuvnogo fetra. Kozhevenno-obuvnaya promyshlennost'. 1998. № 4. s. 44-47.

5. Shvarts A.S., Gvozdeva Yu.M.Khimicheskaya tekhnologiya izdelij iz kozhi - M: 1976. 200s.

6. Zaharova S.V., Slobodskih L.V., Gluhovtsev V.G., Tsivinskaya L.K. Primenenie furanftororganicheskih soedinenij v kremnijorganicheskih kompozitsiyah. Kozhevenno-obuvnaya promyshlennost'.1995. № 1-2. s.25-26.

7. Sintezy ftororganicheskik soedinenij / Pod red. akad.I.L. Knunyantsa i prof. G.G. Yakobsona.-M: Khimiya, 1973. s.144.

8. Patent RU 2000336, 1993.

9. G.M. Brooke, J. Fluorine Chem., 1997, v. 86, № 1, p. 1-76

10. N. Isikawa. Y. Kobayasi. Ftor. Khimiya i primenenie. –M.: Mir, 1982. s. 149-150.

11. A. Pittman. Poverhnostnye svojstva ftoruglerodnyh polimerov, v kn: Ftorpolimery.-M: Mir, 1976. s. 340.

12. Soedineniya ftora: Sintez i primenenie: Per. s yapon. /Pod red.N. Isikawa.-M.: Mir. 1990. s. 158.