Application of Fragrance Retanning Agent

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Abstract: The fragrance retanning agent (FRA), previously prepared in our laboratory, was used in retanning wet blue goatskin. To contrastively evaluate odor reservation of FRA and lemon perfume on retanned leather, the flavor compounds volatilized from treated leather were analyzed by sensory test and GC-MS. The results show that the odor reservation of leather treated with FRA is significantly better than that treated by lemon perfume directly. Due to peak areas of flavor compounds volatilized from fresh side are larger than from grain in GC, the FRA mainly penetrates from fresh side into leather during the retanning process. To comparatively observe the effects of FRA and Levotan L (a commercial polyurethane resin) on retanned leather, the physical and mechanical properties of leather were measured, such as tensile strength, elongation and tear strength. The leather retanned with FRA shows improvement in fullness and tightness. Also, the results show small improvement in tensile strength and tear strength, but fall in elongation. In a word, FRA as a new functional material can both satisfy the requirements of perfumed finishing and retanning for fragrance leather.

Key words: leather; functional finishing; retanning agent; fragrance; GC-MS

1 Introduction

Since the 21st, with the improvement of living conditions, people propose more requirements on leather products, such as comfortable, healthy, funny and unique. The trend of functional finishing has been raised more concern in leather industry. Taken fragrance finishing for example, the perfume not only confers aroma to leather, but also can be used as preservatives, antiseptic, deodorizer and so on. Thus, fragrance finishing can vary leather products style and expand applications, as well as greatly enhances the added value.

Over the past several years, the study of fragrance finish has focused on the following two aspects. One, sulfited and oxidized oils were mixed with perfume and stabilizing agent for leather fatliquors, and then leather had aroma smells with the penetration and distribution of fatliquors into leather interior [1]. The other, perfume encapsuled with micro-capsule technology was used in fragrance finishing by coating process [2]. However, few researches about retanning material as filler for fragrance leather have been reported.

In the present work, we have focused on the effects of a fragrance retanning agent (previously prepared in our laboratory) on wet blue goatskin.

2 Experimental

2.1 Materials

The wet blue goatskin was prepared in a tannery. The fragrance retanning agent (polyurethane resin, solid content is 39% (w/w), pH of 10% FRA solution is 4.5～5.0) was previously prepared in our laboratory. The Levotan L (a commercial polyurethane resin, solid content is 34% (w/w), pH of 10%

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Levotan L solution is 6.0) was purchased from Bayer Company, Germany. The lemon perfume was purchased from Shanghai Apple Perfume Corporation (terpene perfume oil).

2.2 Application procedures

Matched pieces of wet blue goatskin (15×20cm) were taken from the back and flank areas of the tanned skin. The chemicals used in the following procedure were based on the weight of the leather. The leather pieces were first rehydroted in a 400% float containing 0.5% peregal at 35℃ for 30 minutes, and then the float was drained, after this step the samples were respectively neutralized to pH 5.0 and pH 6.5 in a 150% float containing HCOONa and $NaHCO_3$ at 35℃ for 40 minutes. In the retanning step, 3%FRA was added in a fresh 200% float at 35℃ for 1.5hr. The retanning materials used were 3% Levotan L and 1.5% lemon perfume as control. Then, the samples were air-dried and staked.

2.3 Evaluation of Odor Reservation of FRA on Retanned Leather

2.3.1 Sensory Test

The leathers treated with FRA and lemon perfume were roasted in oven at 50 ℃ for 4hr. the leather samples was smelled directly, and the leather odor was evaluated by using sensory test as shown in Tab.1[3].

Tab. 1 Six-point scale of the odor reservation method

Odor	Undetectable	Just detectable (threshold dilution)	Distinct and well-define odor (recognition threshold)	Easily noticeable	Strong	Very strong
Scale	0	1	2	3	4	5

2.3.2 GC-MS Instrumental Analysis

Headspace conditions: Equilibrium temperature 80℃; equilibrium time 10min; transmission line temperature 110℃; carrier gas: He gas; flow rate: 1ml/min.

Chromatographic conditions: Capillary Column: TR-5MS weak polarity column, 30m × 0.32 mmID × 0.5um (USA Thermo Electron); carrier gas (He) flow rate:1.0ml/min; constant column temperature: initial temperature 50℃, keeping 1 min, temperature ramps of 10℃/min to 230℃, keeping 10min; injection port temperature 240℃; no triage; transmission line temperature of 250℃.

MS conditions: electron impact (EI) ion source; electron energy 70eV; solvent delay 5min; ion source temperature of 200℃; full spectrum scanning; quality scanning range m/z 50 ~ 400.

Experimental steps are as follows:

The leather samples, respectively treated with FRA and lemon perfume in pH5.0 and pH6.5, were staked and air-dried, and then heated in oven at 50 ℃ for 4hr and naturally cooled down. The samples were splitted to two layers (labeled fleshed side and grain side, thickness of each layer was about 0.4mm) by using Precision Splitting Machine. First, these layers were cut into splinter, and then 1.000g splinter were accurately weighted and placed in a 20 mL headspace bottle. Next, the bottles were sealed with rubber gasket and aluminum cap, after this step the bottles were placed in Headspace Auto sampler and analyzed by Trace GC/DSQ GC-MS (Thermo Electron Company, USA).

The volatile compounds from retanned leather were isolated and then identified with Xcalibur™ software, combining NIST2005 spectrum database and manual searching. The integrated areas of individual peaks in gas chromatogram were used as an evidence to evaluate the odor reservation of FRA on retanned leather and the distribution of FRA and lemon perfume on flesh side and grain side.

2.4 Characterization of Leather Retanned with FRA

2.4.1 The Thickness and Shrinkage Temperatures

Leather samples were measured with a thickness gauge after the rewet step and again when the retanning process was finished. The increase in thickness was calculated using the following formula:

$$\triangle T(\%) = \frac{T_1}{T_0} \times 100\% \quad (1)$$

Where T_1 is the thickness after retanning and T_0 is the thickness before retanning.

Shrinkage temperatures of retanned leather samples were determined by ASTM method D6076-97[4]. A 5.0×40mm specimen was cut from each leather sample. The specimens were inserted into the bath of glycerin (75%) and water (25%). The bath was heated at a rate such that the rise in temperature was maintained at 3℃ per minute and the temperature at the first definite sign of shrinking was recorded.

2.4.2 Sensory Properties

Sensory test was taken in terms of fullness, tightness, softness and non-loose grain by hand and visual examination.

2.4.3 Physical Properties

The physical test of these retanned leather test samples were made by cutting the samples from official portions of experimental leathers with the use of metal dies and these cut samples were conditioned for about 48 hours at temperature 20℃ and 65% relative humidity. These conditioned samples were tested for tensile strength, tear strength and elongation on Automatic Strength Tester AI-7000S at speed 100mm/min[5].

3 Results and discussion

3.1 Odor Reservation of FRA on Retanned Leather

Due to the lemon perfume mainly contains terpenes, such as limonene, myrcene, triazene aldehydes, alcohols, etc[6]. Therefore, the compounds which showed obvious peak in gas chromatography were selected to evaluate the effects of retanning agents on odor reservation, including: β-pinene, limonene, terpinene, myrcene, linalool, nonanal, citral a, and citral b.

According to the integrated peak areas of each compounds separately volatilized from fresh side and grain side in Fig.2, it shows that although materials and pH are different in the retanning process, the smell volatilized from fresh side are much more than that from grain side. In other words, the lemon perfume is mainly distributed in fresh side of retanned leather. This results would imply that in the retanning process, FRA mainly penetrates from fresh side into inner leather. This may be related with the size scope of FRA, the fibers weave in fresh side are so relatively loose that be helpful for permeation of FRA.

By comparing “a” and “b” in Fig.1, it is shown when pH was 6.5 in the process, the total integrated peak area of compounds from leather retanned with FRA are larger than that treated with lemon perfume. This indicates that after heating treatment, the odor reservation of FRA on retanned leather are significantly better than that of directly treated with perfume. From the comparison between “c” and “d”, it can be seen that the peak areas of compounds are similarly equal, except the β-pinene and limonene in “c” are higher than in “d”. These suggests that when the process of pH is 5.0, from the effect of odor reservation, the FRA on retanned leather is slightly better than the lemon perfume. As to the contrast of “a” and “c”, the peak areas of volatilized compound in pH 6.5 are significantly higher than that in pH5.0. It would be indicated the pH prefers 6.5 to 5.0 in application of FRA.

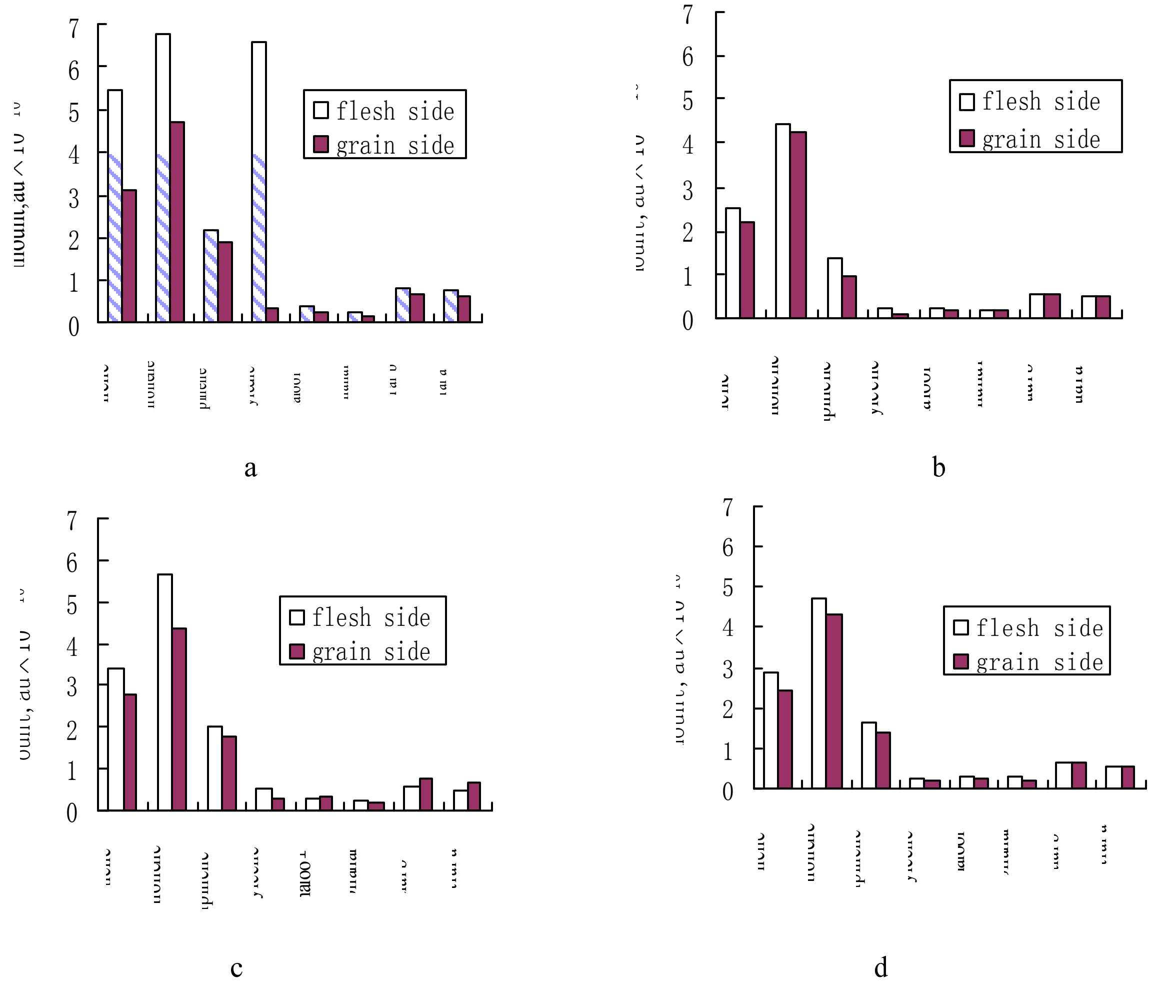

Fig.1 Distribution for main compounds of residual perfume in leather

Note: "a"=leather samples retanned with FRA at pH 6.5, "b"= leather samples retanned with lemon perfume at pH 6.5, "c"= leather samples retanned with FRA at pH 5.0, "d"= leather samples retanned with lemon perfume at pH 5.0.

Attentively, the above experimental results are consistent with the results obtained from sensory evaluation (see Tab. 2).

Tab. 2 Sensory evaluation of odor reservation of FRA on retanned leather

	FRA		FRA		Lemon perfume		Lemon perfume	
	pH 5.0		pH 6.5		pH 5.0		pH 6.5	
Side	Fresh	Grain	Fresh	Grain	Fresh	Grain	Fresh	Grain
Scale	2	1	2	2	2	1	1	1

The reason for above experimental phenomena may be that FRA as a new functional material can control fragrance slow-release. Compared with fragrance treatment by solely adding perfume, the odor reservation time of FRA is longer. Moreover, due to its weak positive electricity, FRA is applied in slightly high pH conditions to enhance the bonding fastness of leather fibers and FRA. However, excess high pH will lead to bonding increase, and even cause mass FRA to sedimentate on surface. When the application system pH is 6.5, just close to isoelectric point (6.7-7.0) of chrome tanned leather, the relative balance of FRA combination and penetration in leather samples may be achieved.

3.2 *The Retanning Effects of Leather Treated with FRA*

As shown in Tab. 3, the shrinkage temperature of samples treated with FRA is slightly higher (3-4℃), but no significant advantages were observed, suggesting that FRA may be capable of coordinating with the chrome from tanned leather to form unipoint or multi-point covalent bound. Obviously, the combination is weaker than the reaction between Levotan L and chrome. Besides, The effect of FRA and Levotan L on leather incrassation rate before and after retanning was studied, FRA slightly make leather thicker, but not markedly as good as Levotan L. In addition, from the effect of different pH conditions on leather shrinkage temperature and thickness, the thickness increase rate of leather treated with FRA in pH 6.5 is higher than that in pH 5.0, but no impact on shrinkage temperature.

Tab. 3 Shrinkage temperatures and thickness of retanned leather

	Blank	FRA pH5.0	FRA pH6.5	Levotan L pH5.0	Levotan L pH6.5
Shrinkage temperatures (℃)	118	122	121	125	126
Increase in thickness (%)	2.1	8.8	10.3	30.5	28.1

Among the measures of both retanning and lubricating ability for any retanning product, strength properties are considered to be important. Tab. 4 shows the physical test results of retanned leather samples, respectively treated with FRA and Levotan L in pH = 5 and pH = 6.5. It can be seen that FRA can slightly increase tensile strength and tear strength, but fall in elongation. These results are consistent with the disadvantage of softness in sensory test.

Tab. 4 Physical properties of retanned leather

	Blank	FRA pH5.0	Levotan L pH5.0	FRA pH6.5	Levotan L pH6.5
Tensile Strength (N/Mm^2)	6.42	7.25	9.98	7.62	7.49
Elongation (5N) (%)	29.42	29.05	34.76	29.15	39.33
Tear Strength (N/Mm)	49.37	49.51	49.35	54.96	49.31

As to the sensory test for retanned leather, although the effects of FRA on leather are no better than that of Levotan L, FRA can improve the fullness and tightness of leather. Furthermore, with the raising of application pH value (from pH 5.0 to pH 6.5), the softness and fullness of leather increased slightly, while the tightness and non-loose grain is virtually unchanged.

4 Conclusions

This study represents the effects of a fragrance retanning agent used in wet blue goatskin (the retanning step was that 3%FRA was added in a fresh 200% float at 35℃ for 1.5hr under pH 6.5). The results present that FRA mainly penetrates from fresh side into leather and the odor reservation of leather treated with FRA is significantly better than that treated by lemon perfume directly. Furthermore, compared with a commercial retanning agent, FRA also can meet the retanning effects. Above all, FRA as a new functional material can both satisfy the requirements of perfumed finishing and retanning for fragrance leather.

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Reference

[1] K.Y. Wang; B. Sun; H. L. Zhou; et al. china leather, 2004, 17.

[2] Kleban Martin; Weisser Jurgen; Koch Friedrich; et al. Leather finished with scent-containing microcapsules [P]. US:2006216509, 2006-09-28.

[3]Kyoji sato; Akira Okumura; Toshinori Inatsugi; et al. A Consideration Of Evaluation Method For Leather Odor, The 7th Asia International Leather Science And Technology Conference, 2006.

[4]ASTM. Annual Book of ASTM standards, Vol, 15-04.General Products, Chemical Specialities and End Use Products. 1997: 638-640,.

[5] W. Q. Jiang. The Analysis of Leather, Beijing:Light Industry Press,1999,82-91,96-102.

[6] B. G. Sun; J. He. The Perfume Chemistry and Techniques, Beijing: Chemical Industry Press, 2004, 65-68.