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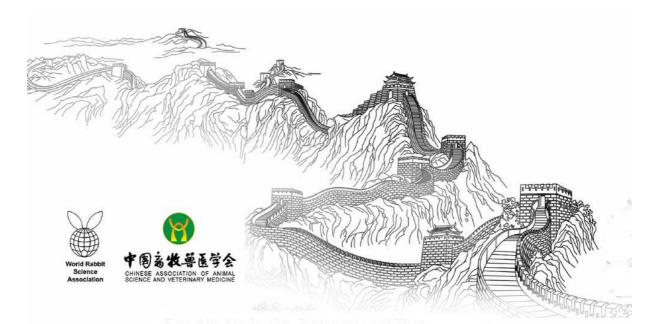
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INNOVATIVE PROCESSING TECHNOLOGIES FOR RABBIT SKIN AND HAIR

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ABSTRACT

Rex skin having marten fur feature and silky touch is regarded as one of the most common used fur raw material. However, tanning process of rex skin is continuing to use traditional formaldehyde tanning for rabbit skin in China, that causes a serious environmental pollution and vast sewage, the resultant fur harming the hearth of consumers. So the novel research is focused on the formaldehyde-free and/or chrome-free tanning, clean rabbit dyeing processing technology, as well as biotechnology .Rabbit hair, a silky and delicate fibre, prized for it its fineness, softness, snowy-white color, and excellent thermal insulation characteristics, has received special attention as a precious raw material in textile industries. However, due to lower flexibility and reducing inter-fiber cohesion caused by it scale structure and ladder type medulla, mechanical processing for rabbit hair textile is difficult, especially for high-quality and fashion textile goods. In the current research, a creative solution to producing high quality rabbit hair textile without destroying its inherent good properties was introduced, involved in novel processing of carding for spinning pure rabbit hair yarn and anti-hair-losing finishing, which have been proven effective and economical by manufacturer of producing rabbit hair garments in China.

Key words: Rex skin, tanning, rabbit hair, carding machine, anti-hair-losing finishing.

INTRODUCTION

Current in China, people are encouraged to work hard to improve their living stander by the government, and Chinese peasant may found that it is a good way to make a better life by breeding rabbits, since the skin, meat and hair of rabbit have commercial value, while the investment of breeding rabbit is not big. As a result, rabbit fur and hair are produced in very large quantities and China is the leading producer in the international rabbit fur and fiber market, so there is an urgent need for developing new products and creation of market of rabbit skin, fur and hair. However, tanning process of rabbit skin and fur is continuing to use traditional formaldehyde tanning in China, that cause a serious environmental pollution and vast sewage, the resultant rabbit fur harming the hearth of consumers. In order to solve these problems, many new technologies have been developed.

As one of the finest animal fibers, rabbit hair is a kind of good textile material with its well known reputation for fineness, lightness, softness and excellent thermal insulation (Mahapatra, 2010; Ammayappan, 2007). However, the very smooth fiber surfaces with few cuticles scales causes low bonding force between fibers and rabbit hair easily falling off from fabric during wearing, which severely limit the development of rabbit hair products (Mahapatra, 2010; Zhen *et al.*, 1994; Wu and Ji, 1998). Some effort has been done by authors to develop rabbit hair fabric with better performance and high add value, involving improvement of spinning ability of fiber by creating new carding technology and hair-losing resistance by chemical finishing, this would be present in the paper.

In this paper, innovative processing technologies for tanning of rabbit skin to rabbit fur are reviewed in part 1, while some novel technology related to rabbit hair processing is introduced in part 2.

PART 1 - INNOVATIVE PROCESSING TECHNOLOGY FROM RABBIT SKIN TO RABBIT FUR

1 - Present processing technology for rabbit skin to rabbit fur

Tanning is the decision processing for the performance of fur. The commonly used tanning agent are chrome tanning agent, aluminium tanning agent, formaldehyde, glutaraldehyde, oil tanning agent and various organic synthetic tanning agent. Nowadays Domestic rex skin tanning technology still use formaldehyde or formaldehyde-aluminum tanning technology for rabbit skin with low value. The fur tanned with aldehyde is characterized with the pure white hair, a soft and light skin and good oxidation resistant. The disadvantage of formaldehyde tanning is that the free formaldehyde in fur is as high as 300mg/kg which has great harm to customers. Besides, subcutaneous tissue of rabbit skin is a layer of dense muscle membrane tissue. The operator has to peel it off with hand in order to let chemicals added to penetrate into the skin which increase the labor work of the processing. The chemicals used in degrease process also lead to a large amount of pollution.

Chromium-tanning, formaldehyde tanning or aldehyde-aluminium combined tanning leads to a serious environmental pollution, and the final products contend volatile formaldehyde, which has become the core problem which restricts the sustainable development of the rabbit industry technology.

2 - New processing technologies for rabbit skin

2.1 Chromium-free mineral tanning agents

Nowadays, there are some chromium-free mineral tanning agents, such as aluminium (III) (Fathima *et al.*, 2004), zirconium (IV) (Maltez *et al.*, .2005), zirconium (IV) combined with aluminium (III), titanium (IV) (Peng *et al.*, 2007), or less chromium tanning methods (Covington, 1997). But these alternatives have not been able to replace chromium for various reasons. Aluminium (III) is only a pseudo transition metal ion which forms outer orbital complexes with poor stability resulting in reversible tanning. So conventional aluminum tanning is characterized by its poor wash fastness, hard to store, hair slip on the fur and hardening of fur. Zirconium (IV) and titanium (IV) are d0 metal ions, whose crystal field stabilization energies are zero and hence, also produce reversible tanning. Zr (IV) is also acidic and has the tendency to polymerize extensively even at low pH conditions damage hair.

During the past few decades combination tannages have been developed to avoid the use of chrome, such as tannages of vegetable tannins with aldehyde compounds or with metal tanning agents (Madhan *et al.*, 2005; Shi, 2006a; Shi, 2006b). Among these tannages, the combination of vegetable tannins and aluminium (III) is a promising option that produces leathers with high hydrothermal stability comparable to that of chrome-tanned leather.

2.2 Organic tanning agent

Conventional organic tanning agent does not meet the requirements of the fur, but it is used in the retanning, improving the performance of the leather. In order to produce chromium-free and formaldehyde free fur product, many efforts are tried to develop a variety organic tanning agent, shown as following.

- (1) Organic phosphonium tanning agent. The composition of organic phosphorus tanning agent is tetra-hydroxymetyl phosphonium sulfate. The application of organic phosphate tanning technology on rabbit skin and tanning performance of different phosphate were studied by our research team (Li et al., 2011), the result shows the shrinkage temperature of tanned rabbit skin reaches 84°C to 89°C. But there are some problems in its application in rabbit skin. The color of the final fur products treated with organic phosphonium tanning agent will become yellow and the luster and strength of the hair are poor due to the oxidation followed with retannage. At the same time, finished products may release free formaldehyde.
- (2) F90 produced by Clariant : F90 is a kind of organic tanning agent without chromium and formaldehyde. Its application in rabbit fur tanning by us showed that the color of the fur retanned with F90 is pure white, and the physical properties are good, Ts reaches 72°C. But the usage amount of retanning agent is over 10%, which leads to high cost.
- (3) X-tan produced by LanXESS : It is a kind of sodium sulfonate organic agents with amino- formoxyl group. This organic agent can react with the peptide side chain amino, only release CO_2 and water, so it is an ecological tanning agent. The reaction mechanic shows from Figure 1 (Chris Tysoe, &Dr. Marc Hombeck).

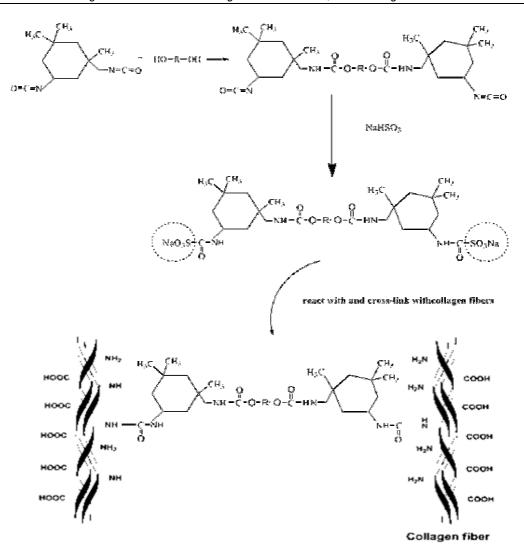


Figure 1 Diagram of the reaction mechanic between sodium sulfonate and collagen fibers

Based on this principle, we developed FTA retanning agent with aliphatic di-isocyanate in our laboratory. FTA is a new ecological organic tanning agent. The best optimal tanning conditions of FTA were determined. The experiment results showed that the dosage of FTA is 8g/L, the temperature is 35°C, and tanning for 4 hours basified pH to about 8. The rabbit fur tanned by FTA was soft and white, and the production had strong physical and mechanical properties without formaldehyde detected (Li *et al.*, 2015.).

(4) Polyepoxidetriglycidylisocyanurate (TEPIC)

Polyepoxidetriglycidylisocyanurate (TEPIC) is a tri-functional polyepoxide, that is thought to be one of the most suitable structures for effective collagen crosslinking (Heath *et al.*, 2005). Di *et al.* (2009) investigated the crosslinking behavior of polyepoxide-triglycidylisocyanurate (TEPIC) on dermal collagen and the subsequent characterization of crosslinked collagen matrices. The results showed that TEPIC can be considered as one of the more effective aldehyde alternatives, which could have a potential significance in leather and textile industrial applications (Di *et al.*, 2009; Huang, 2013). Its application in rabbit skin tanning is studied in our laboratory nowadays. The temperature, pH value, dosage used in tanning and time need in tanning process were studied, the physical and mechanical performances were tested. The result shows that rabbit skin tanned with TEPIC has shrinkage temperature $80^{\circ}C \sim 85^{\circ}C$ and with good physical and mechanical performances. The hair and pelt do not have yellowing problem. But the solubility of TEPIC in water is very low so the usage of tanning agents is low and the pollution is heavy.

2.3 Formaldehyde substitute tanning agent

Formaldehyde is a good tanning agent, at the same time it has the function to prevent bacteria growing and hair slipping in soaking process. But formaldehyde is toxic and is forbidden used in fur. There are some

formaldehyde substitutes tanning agent available for fur tanning.

(1) Glutaraldehyde

Glutaraldehyde and modified glutaraldehyde are used for tanning process. But the color of final fur will become yellow and there is free formaldehyde in fur.

(2) Aliphatic aldehyde

Compared with glutaraldehyde, glyoxal is better while the yellowing problem is concerned. While polyaldehyde products such as product TWT or TWS are used, the yellowing problem is not serious. But the physical properties of the fur need further improvement. D-Lysine aldehyde has been studied as novel tanning agent for chrome-free tanning. The result showed that the tanned leather exhibited good fullness, softness, smoothness, color and general appearance compared with which tanned with glutaraldehyde only. And the tanning process using D-Lysine aldehyde reduces generation of toxic waste compared to chrome tanning process and can be regarded as eco-friendly, which reducing the environmental impacts and contributes to the development of greener or cleaner process (Ganesan Krishnamoorthy, 2013)

2.4 Non chrome metal salt tanning agent

Zirconium and aluminum composite tanning agent has been developed in our laboratory. The experiments showed that the tanned rabbit skin is soft and the fur is white. The Ts is above 85°C which meets the requirement of dyeing, so the retanning process is not needed.

3 Other high technologies in the application of fur tanning

3.1 Ultrasonic technology

After a series of studies, ultrasonic cleaner production for rabbit skin has the following advantages: to improve the dispersion of the skin or in a bath of various effective ingredients, remove the useless components of the fur (such as grease and fat, inter fibrillar substance, etc, to promote the combination of active ingredients and fiber of skin, reduce the consumption of chemical materials, reduce production costs and reduce environmental pollution, as a result, the penetration and combination of chemical materials in various process of fur wet process has been greatly promoted, the processing time has been shortened and production efficiency has been improved (Jiang *et al.*, 2006). Ultrasonic technology has been widely reported in wool and leather dyeing. After ultrasonic treatment, the hair dry scale is opened, which is beneficial to the dyeing, the dyeing rate is improved, the dyeing temperature and the time of dyeing are decreased (Wang *et al.*, 2004).

3.2 Alternative carrier medium for sustainable rabbit fur manufacturing

During rabbit fur processing, the chemicals used in rabbit fur manufacturing have to penetrate into the three-dimensional rabbit skin matrix. Therefore, a transporting medium is required to carry the chemicals into the skin matrix (Liu *et al.*, 2002; Sivakumar *et al.*, 2008; Sivakumar *et al.*, 2008). In conventional rabbit fur manufacturing, water is used as the transporting medium to carry the chemicals into the matrix and also as a medium for the reaction between the chemicals and the functional groups present in skin matrix (Beinkiewicz, K. 1983). Therefore, water plays an important role in fur manufacturing. Though water has an important role in fur manufacturing, the average uptake of chemicals in aqueous medium is only about 65% to 75%, which leads to generation of wastewater with high pollution load.

In order to solve this problem, three alternative carrier medium to water have been proposed as green approaches, named green organic solvents, supercritical fluids and switchable solvents.

Organic solvent as medium for tanning and dyeing

There are several kinds of organic solvents which have been applied for tanning process. Acetone is used to dehydrate the delimed bovine leather to obtain dehydrated-pelt with the optimal physical and chemical characteristics that will allow its subsequent tanning by immersion processes in aqueous solutions of chemical (Anna *et al.*, 2015). When compared to existing traditional processes, there are economic and environmental advantages resulting from the use of this new system. More specifically, the new process results in reductions of 30.6% in water use, 50.2% in chemical use and 16.4% in process time. In addition, a reduction of 27.3% in wastewater and a reduction of 47.5% of thermal energy consumption are obtained. However, this new system presents an increase in electricity consumption of 63.03% and an increase in gaseous emissions of 75% due to the use of acetone in the dehydration process and the 0.5% losses of acetone during the process.

Trichloroethylene is also used in the tanning process of rabbit skin. The result showed that the moisture content of pelt is about 40%, the ratio of trichloroethylene, isopropyl alcohol and water 95:1:0 or 90:1:9 and the chromium powder 5g/L gave the optimum tanning effect. The good fibers dispersion is obtained and Ts of tanned rabbit fur is $95^{\circ}C$ (Liu *et al.*, 2014; Li *et al.*, 2013).

Supercritical CO₂ fluid technology

Supercritical fluid is a liquid at a certain temperature and pressure. Carbon dioxide supercritical fluid is widely used because of its chemical inertia, low cost of raw materials. It is not toxic, recyclable and not flammable. Supercritical CO_2 has been or may be applied to the process of fur, such as degreasing, tanning, dyeing, etc. When chrome tanning of the rabbit fur is carried out in CO_2 a super critical condition, the supercritical fluid replaces water as the medium to achieve the transfer of the skin in the acid skin. The biggest advantage of this technology is to achieve "zero emissions" and the full absorption of chromium is achieved. But the processing is carried at high pressure, the industrial application is limited (Liao *et al.*, 1999).

Switchable solvents

Switchable solvents are a new green approach that is now emerging to facilitate both reaction and subsequent product separation. Switchable solvents are defined as solvents that reversibly change their physical properties instantly. This property is a consequence of a reversible reaction in response to an external stimulus such as change in temperature, and the addition or removal of gas (Pollet *et al.*, 2014; Jessop *et al.*, 2012). Because of the reversibility of the reaction, the switched solvent can easily be brought back to its original state. Switchable solvents are mainly based on amine, amidine and mixture of amine/amidine based compounds. Usage of switchable solvents in leather and fur processing has not been studied so far. Phan *et al.*(2009), and Samori *et al.*(2013) have studied switchable solvents for oil extraction from soya and biodiesel from algae. The same principle could also be applied in rabbit fur making thereby turning fur processing green.

In conventional method of degreasing process, fat molecules are removed from the skin matrix in the form of emulsion, whereas in the case of switchable process, the fat molecules can be dissolved by hydrophobic switchable solvents and removed from the skin matrix. Switching the hydrophobic nature of solvent to hydrophilic can separate dissolved fat molecules. Generally, carbon dioxide, nitrogen and heat are used to trigger switchable solvents.

There are several advantages of using switchable solvents in rabbit fur processing, such as switching the hydrophobic nature to hydrophilic leads to separation of fat and solvent layer, solvent layer can be recycled and reused, water is not necessary and energy required for solvent and solute separation is very low.

3.3 Nano technology

The research shows that the nanoSiO₂ can obviously improve the strength, wear resistance and anti-aging properties of the resin material if the nano SiO₂ was dispersed in it (Li *et al.*, 2009). If the nano particles are introduced into the tanning agent, the shrinkage temperature and physical mechanical properties of leather is expected to be improved. Skin tanning is realized after the hybridization of inorganic nanoparticles and protein (Fan *et al.*, 2005) and the shrinkage temperature is above 95°C. The nano tanning agent in the future may replace the chrome tanning agent, eliminate chromium pollution, reduce the amount of acid, alkali, salt, and dyes so on. And become a kind of environment-friendly new tanning agent.

3.4 Biotechnology in rabbit fur processing

Enzymes are biodegradable and its application in fur processing can decrease environmental pollution effectively. Nowadays the application of enzymes in soaking, degreasing, pickling and bating are widely studied. The optimum parameters of the acid-enzyme A applied to the rabbit skin in soaking process was studied in our research team. The results indicated that the rabbit wool is firmed on the skin under the optimal amount of acid-enzyme A 0.5g/L, and easy taking lining from the skin. The resultant skin soaked with acid-enzyme A has features of softness, flexible and glossy (Li *et al.*, 2013). The optimum operation condition of alkaline lipase on rabbit skin degreasing process was also studied by our research team (Wu *et al.*, 2013). The results showed that the optimal conditions were determined as follows: temperature 30-35°C, pH is about 7.5, dosages of the lipase at 1 g/L with about 1 h, and better degreasing effect when combined lipase with the degreasing agent, which can destroy the sebaceous glands, and the degreasing speed could be improved effectively.

PART 2 - INNOVATIVE PROCESSING TECHNOLOGY FOR RABBIT HAIR (WOOL)

Novel carding technology for spun rabbit hair yarn

Fibres of the Angora rabbit are very smooth with few cuticles scales, and have low cohesion between fibres, this lead to poor spinning ability of rabbit hair (Mahapatra, 2010). Blending rabbit hair with other fibers is helpful both to exploiting the outstanding positive attributes of each fiber and imparting cohesiveness among fibers. The most popular blend style for rabbit hair is blended with wool in woolen spinning systems, or blended with cotton as well as viscose in the cotton spinning system (Mahapatra, 2010; Ammayappan and Jeyakodi, 2007). Blending

of Angora rabbit hair offers effective means to products rabbit hair spun yarn with speciality performance, but not a solution for spinning fine 100% angora rabbit hair yarn for producing superb soft, light weight and good warmth knitted garments. Fiber modification to increase crimps or surface roughness of rabbit hair is helpful to produce a fine pure angora rabbit hair spun yarn, however, this may increase risk of constant fibre slip out of the yarn as the modification usually cause damage to fiber and extra strength loss of fiber. A novel carding technology specially designed for processing rabbit and utilized in producing rabbit hair spun yarn was suggested and developed. The main characteristic of the carding machine was that filmy web of fibers was stripped off the doffer cylinder by an so-called volume twister instead of doffer comb or tripping rolls which was used in traditional carding machine during carding processing. At the final output of the new carding machine, rabbit hair has been formed into twisted sliver which is readily for drafting and other process for finally yarn. As shown in Fig. 2, the new carding machine for rabbit hair spun yarn is consist of four parts, namely feeding, primary carding, main carding and outputting part.

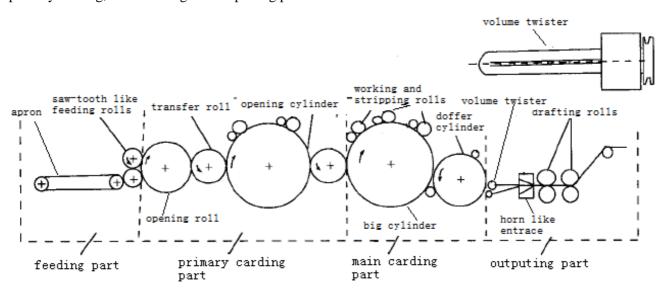


Figure 2. Schematic of new carding machine

The application of new rabbit hair carding machine in China showed that it has the advantages of less damage to rabbit fiber, capability of content of coarse fibers reducing form 5% of raw material to 1% combed material or from 3% to 0.4% with one times carding processing, as well as more than 70% product yield, facilitating the production of fine 100% rabbit hair spun yarns and developing high-grade rabbit hair textile products.

Anti-hair-losing finish by polyurethane emulsion

Rabbit hair's smooth, less crimp texture makes it tend to shed of the fabric and clings to the body who contact it. Surface modification by Enzyme or plasma treatment could lead to coarse surface of the rabbit hair, which may increase the cohesive force between fibers (Danish *et al.*, 2007; Xi 2005; Hou *et al.*, 2006), however, the most important limitation of these processes is causing physical damage to fibers, and treated fabric may appears increasing tendency of losing fibers due to fibers' break-off during the application of the fabric. An alternative ways to achieve hair shedding resistance is using polymeric finish, where interfacial polymerization on the fiber surface of finishing agent or deposition of a preformed polymer from solution and bonds fibers together during later cure process (Pan *et al.*, 2005; Mao and Mao, 2002) by forming a network of bonding points, prevents the rabbit hair from slip off. Therefore, a new process of anti-hair-losing based on the application of a polymer from an aqueous emulsion was researched and developed. The major features of the polymer to be chosen were as following.

- The polymer emulsion should be non-toxic.
- no pretreatment such as oxidation treatment needed when applying the polymer to rabbit hair, since there are cuticle scales on the animal hairs and pretreatment to destroy scales in some degree is usually necessary for such kind processing.
- Low surface tension of polymer emulsion is desired for the purpose of readily spread of the polymer on the fibers surface due to the hydrophobic nature of rabbit hair surface.
- The polymer could be applicable to substrate whereas in forms of sliver, tops, fabric of woven, knitted and

garments.

- The polymer used for the process should be readily prepared from not expensive and commercially available raw materials.
- The polymer should be wonderful elastic in order to avoiding stiffness of the treated fabric.
- The polymer should be high effective in forming a film to guarantee very little dosage when applied to the fabric in the processing.

Polyurethanes appeared to be such a polymer capable of meeting all the physical and chemical demands required for the research (Ney *et al.*, 1976). Anionic self-emulsified aqueous polyurethane was the principal component of the formulation for anti-hair-losing treatment in the present research, while blocked isocyanate was added for permanent finishing effects, since blocked isocyanate will unblocked when it's temperature was raised above 130°C and produce active groups that could react with rabbit hair forming cross-linking structure between rabbit hairs and finishing agent molecules. In addition, poly-acrylate, also a kind of film-forming polymer, was mixed in the formulation with respect to decreasing the finishing cost and increasing water resistance of finishing effects, for poly-acrylate has lower price and better hydrolytic stability compared to polyurethane. A recipe for preparing working liquid of anti-hair-losing treatment is listed in Table 1.

U			
component	compositionpercentage (w/w)		
Anionic aqueous polyurethane (30% solid content)	10-20 %		
Aqueous polyacrylate (30% solid content)	5-10 %		
blocked isocyanate (30% solid content)	5-10 %		
alkylphenol ethoxylates	5-10 %		
triethanolamine	0-0.5 %		
penetrant JFC	0.1-0.5 %		
water	Added to 100% content		

Sodium bicarbonate was used to adjust the working liquid pH at range of 7-8.

Working liquid can be applied to fabrics by padding with an 60-80% wet pick-up and 1.5-3% polyurethane solids on the weight of the fabric, while the optimum amount of polyurethane on a particular fabric will be determined by the type of the fabric and degree of hair-losing resistance required. Exhaustion is an alternative method of the anti-hair-losing treatment of rabbit hair fabric. The amount of polyurethane which should be applied to a rabbit hair fabric to achieve hair-losing resistance may vary between 2 and 5% owf, depending on the property of the fabric and desired finishing effects, while other factors keeping the same as padding ways. The processing procedure is shown graphically in Fig. 3.

Since polyurethane is a kind of elastomeric polymer, the effect on the hand of the treated fabric with such add-on of polyurethane was negligible in the present study. However, soften finishing is recommended to keep the characteristic soft and fluffy hand of rabbit hair fabric, which can be processed according to method usually be taken to treat wool knitted fabrics.

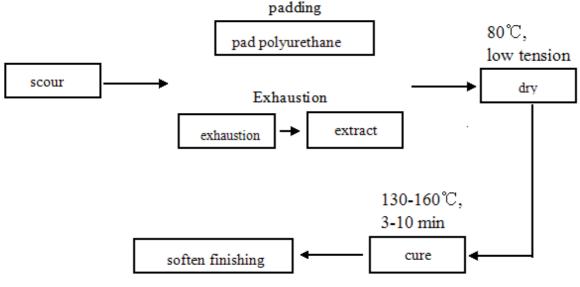


Figure 3. Procedure of anti-hair-losing treatment for rabbit hair fabric **Permanent pressing of rabbit hair fabric treated with polyurethane**

Polyurethane is a kind of multi-functional finishing agent which could affect many aspects of the fabrics' performance. Polyurethane treatment in relation to different properties of the treated fabric are studied, experimental results showed that not only anti-hair-losing property was improved, anti-shrinking, anti-piling as well as crease recovery of the rabbit hair fabric treated with polyurethane emulsion were also observed.



Figure 4 : Durable pressed fabric

What is specially mentioned, the polyurethane treatment also render knitted fabric of rabbit hair crease retention in some extent (Fig. 4 A), which make it feasible to produce durable press garments, although the crease formed is not as sharp as that formed by polyester fabric (Fig. 4 B).

For producing durable press garments of rabbit hair, the polyurethane treated fabric can be left uncured with retaining a latent durable press capability, and could be converted to durable press garments on the garment manufacturer's premises by trimming, shaping on a press, curing and garment constructions .

Dyeing rabbit hair fabric with disperse dyes

Similar to wool, rabbit hair is kind of keratin of fur fibres, usually dyed with acid dye or reactive dyes, has little affinity to disperse dye which is used to dye polyester fiber. While it is possible to submit the rabbit hair fabric treated with polyurethane emulsion to get color in pale or medium shade, since ester group and the hydrophobic soft segment part in polyurethane structure make polyurethane have affinity with disperse dye.

Three kind of disperse dyes, namely disperse red 3B, disperse blue RGFL and disperse red 2BLN, were employed in the research to dye knitted fabric of rabbit hair with polyurethane emulsion treatment, dyeing behavior was studied and compared with that of untreated fabric, and the results were listed in Tab. 2. It can be seen form Tab. 2 that over 50% dye up take and fixation were achieved of textile with polyurethane emulsion treatment in comparison to less than 10% of fabric without the treatment, implying obvious improvement in dye ability of rabbit hair fabric treated by polyurethane emulsion using disperse dye.

Table 2: Dyeing behavior of different rabbit hair fabric using disperse dyes

Samples	Dye up take percentage/%		Dye fixation percentage/%			
	Red 3B	Blue RGFL	Red2BLN	Red 3B	Blue RGFL	Red2BLN
Control	6.95	6.05	9.5	5.42	4.00	7.86
Fabric treated with PU	57.2	61.1	58.2	54.3	56.2	53.1

PU: polyurethane emulsion

The improving dye ability of disperse dye for rabbit hair fabric treated with PU emulsion made it technically possible to producing sublimated transfer print fabric manufactured from rabbit hair with disperse dyes (Fig. 5). Among a number of advantages of transfer printing offered over conventional printing, less water consumption and short-run processes are most notable, which is attractive to manufacturer with the pressure of much consideration to environment. In addition, feasibility of transfer print on rabbit hair fabric using disperse dye might be an option for producing fashionable, interesting and stylized rabbit hair fabrics or garments.



Figure 5. Sublimated transfer print rabbit hair fabric treated with PU emulsion

CONCLUSIONS AND PERSPECTIVES

In order to make the rabbit fur manufacture more sustainable, formaldehyde-free and/or chrome-free tanning are highly focused. The application of supercritical fluids and switchable solvents has great potential for the development of waterless rabbit fur manufacture. Apart from alternate solvent medium, dry tanning approaches to transport the adequate amount of chemicals without any discharge using newer equipment engineering packages need to be explored. These alternative approaches are likely to enhance the cost of rabbit fur manufacture. Considering the impact on environment and currently associated treatment cost, a multi-pronged approach for waterless tanning is essential for a greener and sustainable rabbit fur manufacture.

In order to spun rabbit hair yarn especially spun pure rabbit hair yarn, new type carding machine is recommended. The new type carding machine specific for rabbit hair has the advantages of less damage to rabbit fiber as well as high efficiency of removing coarse fibers, and improvement of value and performance of the final rabbit hair products are expected by applying the new carding technology. The utilization of polyurethane emulsions as described in this paper could increase anti-hair-losing performance of rabbit hair knitted fabric without destroy their desirable properties such as warmth, softness and good water retention. In addition, permanent press property and affinity to disperse dye in some extent was rendered to rabbit hair fabric treated with polyurethane emulsion, possibility of sublimation transfer printing using disperse dye was observed, supplying an option for producing fashionable garments of rabbit hair with interesting appearance.

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REFERENCES

- Ammayappan L., Jeyakodi Moses J. 2007. A comparative study between Angora rabbit hair and Bharat Merino wool. *Man-made Textiles in India, 6, 220-222.*
- Anna Bacardit, Grau Baquero, Silvia Sorolla et al., 2015. Evaluation of a new sustainable continuous system for processing bovine leather. Journal of Cleaner Production.101, 197-204.
- Beinkiewicz, K. 1983. Physical Chemistry of Leather Making. Krieger Pub Co.
- Chris Tysoe, Dr. Marc Hombeck, Dr. Dietrich Tegtmeyer. X-Tan® the innovative organic tanning system.
- Covington, A. D.1997. Modern tanning chemistry. Chemical Society Reviews, 26, 111.
- Danish N, Garg M. K., Rane R. S. et al. 2007. Surface modification of Angora rabbit fibers using dielectric barrier discharge. Applied Surface Science, 253, 6915-6921
- Di Y., Heath R.J.. 2009. Collagen stabilization and modification using a polyepoxide, triglycidylisocyanurate. *Polymer Degradation and Stability*, *94*, *1684–1692*.

Fan Haojun, Li Ling, Shi Bi et al. 2005. Characteirsties of leather tanned with nano si02 JALCA, 100, 22-25.

- Fathima N., Saravanabhavan S., RanhavaRao J. *et al.* 2004. An Eco-Benign Tanning System Using Aluminium, Tannic Acid, Acid, and Silica Combination.*JALCA*,99,73.
- Ganesan Krishnamoorthy, Sayeed Sadulla, Praveen Kumar Sehgal *et al.*, 2013.Greener approach to leather tanning process: D-Lysine aldehyde as novel tanning agent for chrome-free tanning. *Journal of Cleaner Production*, 42:277-286.
- Heath RJ, Di Y, Clara S, *et al.*, 2005. The optimization of epoxide-based tannage systems: an initial study. *J Soc Leather Technol Chem*, *3*, 93–102.
- Hou D.Y., Wei Q.F., Li L.F. 2006. Surface structures and properties of rabbit hair fibers treated with cold gas plasma. *In: Proc. Of 2006 China International Wool Textile Conference & IWTO Wool Forum, 2006 Nov, Xi' an, China, 618-622.*
- Huang Jin. 2013. Study on the modification of collagen and its stability with triglycidylisocyanurate (TGIC). West Leather, 16, 43-51.
- Jessop P.G., Mercer S.M., Heldebrant D.J., 2012. CO2-triggered switchable solvents, surfactants, and other materials. *Energy Environ. Sci.*, *5*, 7240-7253.
- Jiang Lan, LiYa, Shao Shuang-xi *et al.*, 2006.Sound Chemistry Assisted Chrome-free Tannage. *Leather science and Engineering*, *5*, *35* –*37*.
- Li Bin-jing, LIU Gong-yan, WU Fan-hua1 et al., 2013. Study on Chrome Process for Rabbit Skins in the Medium of Organic Solvents. Chinese Journal of Rabbit Farming, 8,8-11.
- Li Min, Wu Lian, ZHOU Yu-ting et al., 2013. The Application of Acid-Enzyme A in Soaking Process of Rabbit Skin. Chinese Journal of Rabbit Farming, (5) 8-11.
- Li Shuang-li, WU Fan-hua, LIU Gong-yan, Zhang Zongcai, 2015. Study on an Ecological Organic Tanning Agent FTA for the tanning of rabbit skins. *Leather science and Engineering, 2, 43-47.*
- Li Yao, Zhou Yuting, Liu Qiang, Zhang Zongcai. 2011. Comparation of rabbit skin tanned by different organic phosphate. *Leather and chemicals*, *6*, *5-7*.
- Li Yun, Ma Jianzhong, Gao Dangge et al., 2009. Development of Chrome-free Tannins . Chinese leather, 11: 51-53.
- Liao Longli, FengYuchuan, Chen Min *et al.* 1999. Study on the Non -pollution Leather Technology Carried outinCO2 Supercritical Fluid Medium(III): study on Leather Dyeing in CO₂supercritical Fluid *.Leather science and Engineering*, *4. 6-12*.
- Liu C.K., Labona L.P., Dimain G.L. 2002. Lubrication of leather with polyethylene glycol. J. Am. Leather Chem. Assoc., 97, 355-368.
- Liu Han, LI Bing-jing, ZHANG Zong-cai, 2014. Study on Chrome Process for Rabbit Skins in the Medium of Organic Solvents. *Chinese Journal of Rabbit Farming*, 6,15-18.
- Madhan B., Gunasekaran S., Narasimman R. et al. 2005. Integrated chrome free upper leather processing Part II: Standardization and evaluation of vegetable-Al tanning system. JALCA, 100, 373.
- Mahapatra N. N. 2010. Processing of rabbit hair fibre in textile industries. Colourage, 1, 68-71.
- Maltez H. F., Carasek E.2005.Chromium speciation and preconcentration using zirconium(IV) and zirconium(IV) phosphate chemically immobilized onto silicagelsurface using a flow system and FAAS. *Talanta:65, 537*.
- Mao Z. P., Mao Y. H. 2002. Modification of rabbit hair fiber with natural polymer. Textile Auxiliaries, 19(6), 17-21.
- Ney E. A., Peake R., Regos N. 1976. Wool Reactive Polyurethanes: A Method For Shrink Resistant, Permanent Press Wool. *Textile Chemist & Colorist*, (8)10, 151-156.
- Pan F.K., Wang S.Y., Long M., et al. 2005. Study on a new method of reducing the water shrinkage of rabbit hair knitted fabrics. J.ofDonghua University, 22(2), 6-8.
- Peng, B. Y., Shi, B., Sun, D. H. et al. 2007. Ultrasonic effects on titanium tanning of Leather. Ultrasonics Sonochemistry, 14, 305.
- Phan L., Brown H., White J. *et al.*, 2009 .Soybean oil extraction and separation using switchable or expanded solvents. *Green Chem.*, *11*, 53-59.
- Pollet P., Davey E.A. et al. 2014. Solvents for sustainable chemical processes. Green Chem, 16, 1034-1055.
- Samori, C., Lopez Barreiro, D., Vet, R., et al., 2013. Effective lipid extraction from algae cultures using switchable solvents. *Green Chem.*, 15, 353-356.
- Shi B. 2006a. Combination tanning of vegetable tannin and aldehydes compound (I):combination tanning of vegetable tannin and oxazolidine. *China Leather*, *17*, *1-4*.
- Shi B. 2006b.Combination tanning Method with vegetable tanninaldehyde compound (II):combination tanning with vegetable

tannin-modified glutaraldehyde. China Leather, 21, 1-3.

Sivakumar V., Gopi K., Harikrishnan M.V., et al., 2008. Ultrasound assisted diffusion in vegetable tanning in leather processing. J. Am. Leather Chem. Assoc., 103, 330-337.

Sivakumar V., Swaminathan G., Rao P.G. *et al.* 2008. Influence of ultrasound on diffusion through skin/leather matrix. Chem. Eng. Process.Process Intensif, 47, 2076-2083.

Wang Aibing, Zhu Xiaoyun, Yang Bin 2004.Ultrasound technology and its application in dyeing and finishing. *Knitting Industry*, 2, 99 –102.

Wu Fan-hua, LIU Shi, ZHANG Zong-cai. 2013. The Use of Alkaline Lipase in the Degreasing Process of the Rabbit Skin. Leather science and Engineering, 23(4), 32-35.

Wu S.J., Ji X.L. 1998. Study on losing fiber of fabrics made of rabbit hairs. *Shanghai Textile Sci. and Tech*, 26(5), 54-56 (*in Chinese*.) Xi B. J. 2005. Modification of rabbit hair fibers by use of enzyme. *Knitting Industries*, 9, 54 - 56. (*in Chinese*)

Zhen W.H., Zbao S.J., Zhuang J., etal. 1994. Study on fiber structure of rabbit hairs. J. of Textile Research, 9, 10-12 (in Chinese).
