Reusing Technologies for Different Leather Wastes

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Abstract: The paper introduced the system of reusing technologies for different leather wastes developed by the authors. The system included preparing regenerated hide from chrome-free leather waste, isolating collagen protein from chrome-containing leather waste by recycling extracting method, preparing collagen protein based leather chemicals and collagen protein composite fiber from chrome-containing leather waste, preparing leather filling & dyeing agent from dyestuff-containing leather waste, and preparing ultra-fine leather powder and its application.

Key words: chrome-free leather waste; chrome-containing leather waste; dyestuff-containing leather waste; leather wastes reusing technologies system

1 Introduction

Leather wastes refer to the waste whose main component is hide collagen structure. According to their origins, leather wastes can be divided into leather waste from tanneries, leather cut waste from leather goods factories and leather waste from the old leather products, and the leather waste from tanneries can be divided into limed hide waste, chrome shavings and crust leather waste.

According to their components, leather wastes can be divided into three kinds mainly:

① Chrome-free leather waste, such as rawhide waste and limed hide waste, which is easy to be reused because of their simple component;

② Chrome-containing leather waste, such as chrome shavings, splitting and trimming waste of wet blue, which is difficult to be reused because of containing chrome;

③ Dyestuff-containing leather waste, such as trimming and cut waste of leather, old leather products, which is very difficult to be reused because of containing chrome, dyestuff, fatliquor and retanning agent.

We have undertaken several programs from the ministry of science and technology, and the national science foundation of China, and developed series of reusing technologies for different leather wastes. The system of reusing technologies will be introduced according to the classification of chrome-free leather waste, chrome-containing leather waste and dyestuff-containing leather waste. The system of reusing technologies for leather wastes is shown as figure 1.

2 Reusing technology for chrome-free leather waste

Chrome-free leather waste can be used to produce high quality collagen protein, such as edible gelatin, edible collagen protein, and collagen protein for cosmetics. This paper introduces a reusing technology to produce regenerated hide from chrome-free leather waste.

The traditional dog chews products are made from splitted limed hide, and the cost is high because splitted hide is the raw material of splitted leather, and during the manufacturing of dog chews many cut wastes are produced. Chrome-free leather waste is very cheap, but it is very small and its thickness is not uniform, so it can not be used to produce dog chews. By the reusing technology developed in the paper, chrome-free leather waste and cut waste can be made into regenerated hide with suitable area and

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thickness, which can be used to produce dog chews products.

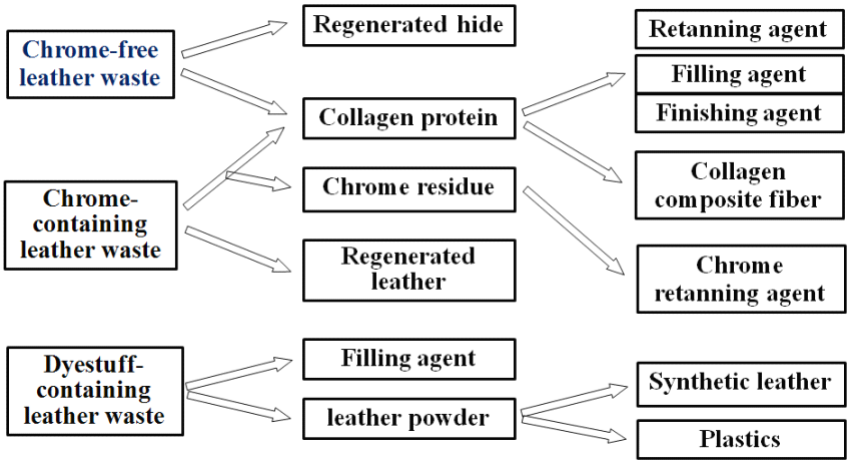

Fig.1 System of reusing technologies for different leather wastes

The reusing technology has following advantages:

① Different chrome-free leather waste can be applied, such as limed hide waste from tanneries, cut waste from dog chews making factories. The utilizing efficiency of making dog chews is improved remarkably.

② The thickness and area are easy to be control by adjusting the technical parameters to meet the demand of dog chews products.

③ The regenerated hide has similar dry strength with splitted hide, and has less wet strength is less than splitted hide, which is suitable for dog chews.

④ Nutrition ingredients can be added conveniently during the preparing of regenerated hide to improve the value of dog chews.

⑤ The cost of regenerated hide is very cheap because the raw material is cheap and the cut waste can be reused.

3 Reusing technologies for chrome-containing leather waste

Series of reusing technologies were developed in the paper to treat chrome-containing leather waste. First chrome-containing leather waste is hydrolyzed to extract collagen protein, then the isolated collagen protein is modified to produce leather retanning agent, filling agent and finishing agent, or to produce collagen protein composite fiber. The chrome residue are used to produce chrome-containing filling agent.

3.1 Isolation of collagen protein from chrome-containing leather waste by recycling method

Generally, the concentration of obtained collagen protein solution by hydrolysis is less than 5%, and the concentration of re-hydrolyzing filtrate of chrome slurry and washing filtrate of chrome cake is less than 3%, so the mixed concentration of collagen protein solution is less than 4%. The concentration is too low, and its disadvantage is the expensive drying cost, and it is uneconomic.b

In the recycling method of the paper, which is shown as figure2, low concentration collagen protein solution, which is from the re-hydrolyzing filtrate of chrome slurry and the washing filtrate of chrome cake, was used to replace water in the hydrolyzing of chrome shavings. The concentration of obtained collagen protein solution can be twice over the obtained collagen protein solution extracted by water. If higher concentration of collagen protein solution is applied, the concentration of obtained collagen protein

solution can be more than 10%, even more than 15% without further concentration, which is very useful to cut down the drying cost of collagen protein powder.

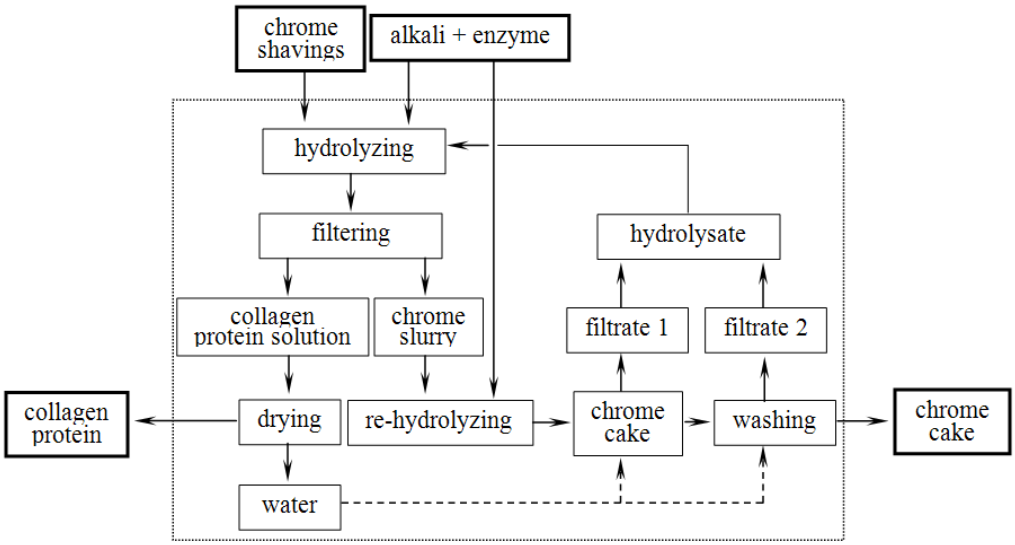

Fig. 2 A recycling method to isolate collagen protein

Chrome component of chrome shavings forms precipitate under the alkaline hydrolyzing condition, and there is still a little chrome solved in the solution which forms the chrome content of collagen protein. The solubility of chrome precipitate is fixed under the condition of same temperature and pH, the amount of chrome solved in the same amount of solution is same, so if the concentration of collagen protein solution is improved to a great extent, the chrome content of collagen protein will be reduced remarkably.

Part of ash content of the obtained collagen protein is from the indissolvable salt, such as MgO, its solubility is fixed under the condition of same temperature and pH, so the ash content can also be reduced remarkably by this method similarly.

3.2 Preparation of Collagen Protein Based Leather Chemicals

The obtained collagen protein from chrome-containing leather waste can be applied as animal feedstuff, but it is much safer to be applied as the raw material of other industrial chemicals. Collagen protein has the good property of moisture absorption and compatibility to human skin, it can be made into retanning agent, filling agent and finishing agent, but chemical modification should be carried out to overcome its disadvantage of bad combinability and water resistance.

3.2.1 Acrylic Resin Modified Collagen Protein Retanning Agent

The active H-containing group can be initiated by radical initiator and copolymerized with aqueous acrylic monomer, such as acrylic acid, methylacrylic acid, acrylamide and acrylonitrile, to prepare protein-containing retanning agent of acrylic type.

The retanning agent from leather wastes has good consistency with leather because of the collagen protein structure, and it can improve the whiten defect, which is very common to the leathers retanned with acrylic resin, because collagen protein is a kind of polyelectrolyte with ampholytic structure

3.2.2 Amine Resin Modified Collagen Protein Filling Agent

The active H-containing group of collagen protein can react with the hydroxymethyl group on the prepolymer of amine resin to form condensation polymer of amine resin and collagen protein. The

condensation polymer can be applied as leather filling agent after further modification by hydrophilic component.

3.2.3 Polyurethane Modified Collagen Protein Filling Agent

The active H-containing group of collagen protein can react with the isocyanate group on the prepolymer of polyurethane to form condensation polymer of polyurethane and collagen protein. The condensation polymer can be applied as leather filling agent after further modification by hydrophilic component.

3.2.4 Phenol-Formaldehyde Resin Modified Retanning Agent

The active H-containing group of collagen protein can react with the hydroxymethyl group on the prepolymer of phenol-formaldehyde resin to form condensation polymer of phenol-formaldehyde resin and collagen protein. The condensation polymer can be applied as leather retanning agent after further modification by hydrophilic component.

3.2.5 Acrylic Resin Modified Collagen Protein Finishing Agent

The collagen protein from leather wastes can be graft copolymerized by acrylate monomers, such as butyl acrylate and methyl acrylate, to prepare acrylate modified collagen protein binder. The defects of bad film forming ability and bad water resistance which are common with protein binders can be improved by the modification. The modified collagen protein binders have the advantages of good vapor permeability, good consistency with leather, and comfortable handle.

3.2.6 Polyurethane Modified Collagen Protein Finishing Agent

The animo and hydroxyl group in collagen protein can react with the active isocyanate group of polyurethane prepolymer to obtain collagen protein modified polyurethane after further chain extension and modification by hydrophilic component, which can be used as finishing agent in leather manufacturing.

3.3 Preparation of Collagen Protein Composite Fiber

Protein fiber is different to natural protein fiber, such as silk and wool, it is a kind of regenerated fiber, which belongs to chemical fiber. Soybean protein and milk protein were studied to produce protein fiber. Collagen protein from the leather wastes is a kind of fibred protein, which has special stick-shaped spiral structure and superior mechanical properties, and is suitable to prepare protein fiber products.

The collagen protein fiber wears comfortable because of the good hygroscopicity and humidity preservation property of the collagen protein. Furthermore, the raw material of collagen protein fiber was from natural animal skin, and its structure is similar to the skin of human body, so the fiber will show good consistency with human body and wears much more comfortable.

3.3.1 PVA Modified Collagen Protein Composite Fiber

Collagen protein of large molecular weight is isolated from leather waste, and is copolymerized with vinyl monomer to increase its soft chain component which is very important to improve its compatibility with the mixed polymer. The modified collagen protein solution is mixed with PVA solution to prepare the dope of PVA modified collagen protein composite fiber.

The dope is de-bubbled under vacuum condition to remove the tiny bubbles in the dope, then is wet spun with the coagulation bath of acidic sodium sulfate solution to obtain primary fiber. The primary fiber is stretched, washed and dried to obtain PVA modified collagen protein composite fiber.

3.3.2 PAN Modified Collagen Protein Composite Fiber

Collagen protein of small molecular weight is copolymerized with acrylonitrile by precipitation polymerization to prepare PAN modified collagen protein which is insoluble in water and soluble in sodium thiocyanate solution.

PAN modified collagen protein and PAN are dissolved and mixed in sodium thiocyanate solution to prepare the dope of PAN modified collagen protein composite fiber. The dope is de-bubbled and wet spun with the coagulation bath of water to obtain primary fiber. The primary fiber is stretched, washed and dried to obtain PAN modified collagen protein composite fiber.

4 Reusing Technologies for Dyestuff-Containing Leather Waste

Dyestuff-containing leather waste is generated after leather is retanned, dyed and fatliquored, so the waste contains chrome, retanning agents, fatliquors and dyestuff, so it is infeasible to isolate pure collagen protein from dyestuff-containing leather waste. The paper introduces two methods to reuse this kind of leather waste, in which chrome, retanning agents, fatliquors and dyestuff are not removed from the waste.

4.1 Preparation of Filling & Dyeing Agent From Dyestuff-Containing Leather Waste

The leather waste is smashed and hydrolyzed under alkaline and boiling condition, most of the collagen protein, dyestuff, retanning agent and fatliquor are isolated from the waste. Part of the fatliquor and retanning agent in the leather waste maybe hydrolyzed. The obtained mixture is dried to prepare leather filling & dyeing agent.

The filling & dyeing agent includes collagen protein, retanning agent, fatliquor and dyestuff, it has the function of filling, fatliquoring and dyeing. If this material is applied in retanning stage of leather manufacturing, the dosage of fatliquor and dyestuff can be reduced by 10~30%. This reusing method has the advantages of low cost and high reusing efficiency.

4.2 Preparation of Ultra-Fine Leather Powder and Its Application

Dyestuff leather waste can be ultra-fine pulverized to prepare leather powder whose size is 5~50μm. The leather powder can be applied in the manufacturing of synthetic leather and plastics products.

The fatal weakness of synthetic leather is bad vapor permeability and uncomfortable handle, ultra-fine leather powder has the same macrostructure and microstructure of natural leather, it can be used to replace wood powder in the manufacturing of synthetic leather to improve its vapor permeability and handle. The application can cut down the cost of synthetic leather and reduce the pollution of leather wastes at the same time.

Some kinds of filling materials are applied in the manufacturing of plastic products to improve their intensity and toughness, or cut down the cost of plastics products. Ultra-fine leather powder is a kind of fiber filling material, can be applied in the plastics products to improve their biodegradability and cut down the cost.

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