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TANNING

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This invention relates to leather tanning and more particularly to an improved process and tanning solution.

Most tanning is done either with chromium salts or by vegetable tanning materials. Synthetic organic tannages are used to some extent. Vegetable tanning materials known as tannins comprise a large group of water-soluble, complex organic compounds which are found in a number of plants. The tannins are commonly divided into two principal classes, namely, catechol tannins and pyrogallol tannins.

The natural tannins differ greatly in chemical composition and in reactions; however, all have the common property of precipitating gelatin from solution and of combining with collagen and other protein material contained in the hide to form leather. The term "hide" is used herein to include smaller animal skins as well as larger animal hides.

All tanning extracts of vegetable origin appear to comprise mixtures of hydroxy phenolic and polyphenolic substances. Synthetic tanning materials which are normally called syntans are used as adjuncts or as partial or complete replacements for natural vegetable tanning extracts. The syntans are generally amorphous, water-soluble materials and include naphthalenic syntans, and aromatic hydroxy syntans. The vegetable tanners most often prefer to use a blend of tanning materials obtained from different plants. Tanning processes have been notoriously slow and this is especially true of tanning methods employing vegetable tannins. Many methods have been suggested and tried to speed up the process of vegetable tanning. While progress has been made in shortening the time required in tanning, it is estimated that the overall tannage time employing the conventional rocker-layaway system is approximately 90 days. In one procedure known as retannage, chrome tannage precedes vegetable tannage. This results in a significant shortening of the time of tannage.

Vegetable tanning conventionally employs a countercurrent process with progressively stronger solutions. The process is usually practiced in a series of large pits in what is known in the United States as the "rocker yard." The name arises from the practice of slowly rocking the hides in the tanning liquors to achieve penetration of the hides by the tanning material. After the tanning liquors have thoroughly penetrated the hides, the hides are then successively placed for a month or more in two or three strong tanning solutions which are known in the United States as the "layaway liquors."

It is the principal object of the invention to provide an improved tanning process utilizing a tannage solution that more readily permeates the hide being tanned.

It is a further object of the invention to provide a tanning process and tanning solution that will reduce the overall tannage time.

The improved tanning method and tanning solution of the invention uses dimethyl sulfoxide, CH_3SOCH_3, as the solvent for the tanning material. Dimethyl sulfoxide has the ability of readily permeating the hide, thus quickly making available tanning material for reaction with the protein of the hide. Dimethyl sulfoxide is a water miscible, polar material. Dimethyl sulfoxide is a powerful solvent which will dissolve most aromatic and unsaturated hydrocarbon including hydroxy phenols and polyphenolics which comprise a large proportion of vegetable tanning agents. Dimethyl sulfoxide is miscible with most of the

common organic solvents such as alcohols, lower ethers, ketones and the like. The process of the invention contemplates the use of dimethyl sulfoxide alone or in combination with water or a miscible organic material as a cosolvent.

Hydroxy benzenes such as catechol and pyrogallol, both of which are found in vegetable tanning materials, have a high solubility in dimethyl sulfoxide. For example, pyrogallol in the temperature range of 20–30° C. will dissolve in an amount of approximately 50 grams in 100 cc. of dimethyl sulfoxide. Dimethyl sulfoxide dissolves 40 grams of naphthalene in 100 cc. of the solvent at a temperature in the range of 20–30° C. Hydroxylated naphthalene materials are even more soluble. Sodium dichromate, which is commonly used in chrome tanning, has a solubility of approximately 10 grams in 100 cc. of dimethyl sulfoxide at 25° C. Sulfur dioxide, SO_2, which is sometimes used in chrome tanning as a reductant for the dichromate tanning solution, is soluble in dimethyl sulfoxide in an amount of approximately 57 grams per 100 grams of dimethyl sulfoxide at 20° C. The various vegetable tannins, aromatic hydroxy syntans and naphthalenic syntans are also readily dissolved in dimethyl sulfoxide.

The solvency power of dimethyl sulfoxide increases greatly with a rise in temperature. Some organic materials which have limited solubility at room temperature become very soluble at moderately high temperatures, say, in the range of 52° C.–79° C. At these moderately high temperatures the solubility of the tannins in dimethyl sulfoxide becomes even greater. The rate of reaction between the tannins and the proteins of the hide will also significantly increase at these moderately high temperatures. The process of the invention may be carried on at room temperatures in excess of 18.45° C., the melting point of dimethyl sulfoxide. Higher temperatures within the foregoing range of 52° C.–79° C. may be used to accelerate the process in some instances.

There is considerable evidence that dimethyl sulfoxide is not only a powerful solvent but is also a desirable reaction medium. It has been demonstrated that the rates of a variety of reactions are greatly accelerated through use of dimethyl sulfoxide as the reaction solvent. This apparent catalytic action, its powerful solvation action and chemical stability make it a very desirable solvent for use in the process of the invention. The material also has a low order of toxicity which, of course, is a desirable characteristic.

As an example of its penetration ability, like pieces of hide of substantially the same thickness were placed respectively in containers of water and dimethyl sulfoxide. The two solvents contained a dye. At the end of a four hour period, the pieces were removed from their respective solvents, cut to expose their cross sections and examined. It was found that the cross section of the dimethyl sulfoxide treated piece was colored throughout. In contrast, there had been little penetration of the water treated hide by the dye.

A vegetable pyrogallol type tannin is employed in the preparation of an aqueous tan liquor having a strength of 25%. In the following examples the tan liquor is diluted with water to give the concentrations indicated.

In this example, the foregoing tan liquid is diluted to provide an aqueous solution of approximately 3% tannins on a weight basis. The same vegetable tanning material is dissolved in dimethyl sulfoxide in an amount needed to provide a 3% weight concentration. Like pieces of a cowhide of substantially the same thickness are placed in the two tanning solutions and left for 24 hours. At the end of the time, the two pieces are removed, cut to expose their respective cross sections and examined. It is found that the dimethyl sulfoxide treated

sample possesses considerable color across its whole cross section. In contrast, the water vegetable tanned piece has substantially no acquired color at its center and less at its outer two faces.

In this example, an aqueous tan liquor having a 10 weight percent concentration of tannins is prepared. A dimethyl sulfoxide solution containing 10 weight percent of the same vegetable tanning material is also prepared. Two equal sized pieces having approximately the same thickness are cut from a cowhide and placed respectively in the two tanning solutions. The two pieces are left in their respective tanning solutions for four days and then removed, cut across their respective cross sections, and examined. The dimethyl sulfoxide treated piece clearly shows a greater degree of tanning than the piece from the aqueous tanning solution.

In this example an aqueous tan liquor having a 10 weight percent concentration of synthetic tanning material is prepared along with a dimethyl sulfoxide solution of like concentration of the same tanning material. The particular synthetic tanning agent used is an aromatic hydroxy syntan. Two equal sized pieces of approximately the same thickness are cut from a sheepskin and placed respectively in the two tanning solutions. At the end of four days, the two pieces are removed from their respective tanning solutions, cut across their respective cross sections, and examined. Again, the dimethyl sulfoxide treated piece shows a greater degree of tanning than the piece from the aqueous tanning solution.

The dimethyl sulfoxide may be removed from a tanned leather by leaching in a water bath.

Although exemplary embodiments of the invention have been disclosed and discussed, it will be understood that other applications of the invention are possible and that the embodiments disclosed may be subjected to various

changes, modifications and substitutions without necessarily departing from the spirit of the invention.

I claim:

1. A method of tanning comprising:
providing a tanning solution containing dimethyl sulfoxide as a solvent and a hydroxy aromatic tanning agent as solute;
holding a hide in the tanning solution for a period of time required to impart the degree of tanning desired.

2. A method of tanning comprising:
holding a hide in a dimethyl sulfoxide solution of a vegetable tanning material for a period of time required to impart the degree of tanning desired.

3. A method of tanning comprising:
holding a hide in a dimethyl sulfoxide solution of a hydroxy phenolic tanning material for a period of time required to impart a degree of tanning.

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