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SYNTHETIC TANNINS FROM SULFOMETHYLATED YACCA GUM AND PROCESS OF TANNING THEREWITH

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This invention relates to a new tanning agent and to a new method for tanning hides and skins using the new agent.

Water soluble synthetic tanning agents have long been desired by tanners because of the chemical and physical uniformity obtainable with synthetic products which would allow simple control of the tanning process and reproducibility of results in tanning. Furthermore, readily available synthetic tanning agents are desired as replacements for natural tanning agents because the latter are becoming scarce and their continued regular supply is not assured. However, water soluble synthetic tanning agents developed in the past have either been too expensive for general acceptance or have not provided leather which is the equivalent of that obtained with natural tanning agents, e. g. vegetable tannins.

It is a feature of this invention to provide a new inexpensive and readily available tanning agent, the tanning agent being effective according to the methods taught herein to tan hides and skins to form leather products similar to leather tanned with natural tanning agents.

According to the present invention yacca gum is treated chemically to form a reaction product which is water soluble even in a strongly acid medium and is useful as a tanning agent. The treatment involves the reaction of yacca gum with an aldehyde and certain alkali metal salts of sulfurous acid in relative proportions which have been discovered to produce the new tanning agent.

The tanning process of the present invention involves treating hides or skins in the condition normally encountered in tanning, as in bated or pickled condition, with water solutions of these yacca gum reaction products which serve as tanning agents when maintained at a suitable acid pH.

The tanning agents of the present invention are prepared by converting normally water insoluble, alcohol soluble yacca gum to a condition where it is soluble even in strongly acid water solutions by treating it with an aldehyde and certain alkali metal salts of sulfurous acid which are believed to act to sulfomethylate a portion of the gum thereby rendering it water soluble.

Yacca gum is a water insoluble, alcohol soluble, naturally occurring resinous product obtained from xanthorrhoea plants and is variously known as yacca gum, gum accroides, acaroid resin, botany bay gum, etc. It has not been considered suitable as a tanning agent because of its inherent water insolubility and its inherent high color. Its water insolubility precludes its use in normal tanning procedures which are carried out in an aqueous medium, and furthermore when it is attempted to tan hides and skins with yacca gum carried in an organic solvent the color referred to is imparted to the hide or skin. Yacca gum is believed to comprise the p-coumaric ester of a resinotannol, e. g. erythroresinotannol, to the extent of 80% to 85% and to contain various other ingredients in minor proportions. Its molecular weight is taken to be 826 for purposes of calculation herein.

We have discovered that it is important to maintain the relative proportions of the special reagents named above within certain limits to effect the conversion of yacca gum to a water soluble reaction product which remains water soluble even at the low pH's used in tanning and which tans hides and skins to light colored leathers having properties similar to vegetable tanned leathers.

Certain alkali metal salts of sulfurous acid, including alkali metal sulfites, alkali metal bisulfites, and certain special bisulfites, e. g. alkali metal metabisulfites, formaldehyde alkali metal bisulfites and formaldehyde alkali metal metabisulfites, have been found to react with proper aldehydes and yacca gum to form the water soluble reaction product of this invention. For purposes of calculation it should be noted that the sulfites and bisulfites each contain one mole of $—SO_3$ per mole of the ingredient, whereas the metabisulfites each contain 2 mols of $—SO_3$ per mol. When an alkali metal bisulfite or metabisulfite is used, it is important that a suitable alkaline material be present to provide an alkaline reaction medium in which a suitable water soluble reaction product can be prepared.

Various aldehydes can be used in the present reaction but for reasons of ease of handling and economy, formaldehyde, paraformaldehyde and formaldehyde alkali metal bisulfites and metabisulfites are preferred.

It is believed that yacca gum is rendered soluble according to the present invention through sulfomethylation of the resinotannol ester which forms the major component of the yacca gum. Thus the aldehyde and the alkali metal salt of sulfurous acid apparently react together in equimolar proportions and add to the resinotannol as a $—CH_2SO_3Na$ group which renders the resinotannol ester and therefore the yacca gum, water soluble. Upon acidification of the sulfomethylated resinotannol ester the sodium present on the added group is replaced with hydrogen. Further aldehyde above a molar proportion equivalent to the molar proportion of the sulfite generally is incorporated in the reaction batch to assure that the reaction will take place to provide a water soluble tanning agent, and also to provide a slight increase in the average molecular weight of the resinotannol through cross linking, i. e. by means of $—CH_2$-cross linking groups. The degree of cross linking can be controlled by regulation of this excess of aldehyde.

The above explanation is advanced as of possible assistance in understanding the invention. Nevertheless it is to be understood that the subject-matter claimed is the reaction products, and the methods of using them for the tanning of skins and hides, and patentability of the product or methods is not dependent on the correctness of the explanation of the mechanism of reaction.

The preferred procedure for preparing the tanning agents of the present invention comprises dispersing finely divided yacca gum and a proper alkali metal salt of sulfurous acid in water with stirring, adding an aldehyde to the resulting dispersion and heating this reaction batch, with stirring, at elevated temperatures, e. g. 70° C. to 110° C., to cause reaction of its ingredients. When a sample taken from the reaction batch does not become turbid, i. e. show signs of precipitation, upon being cooled and acidified, for example with 33% sulfuric acid, to a pH of 2.5, the reaction batch is allowed to cool and is neutralized with 33% sulfuric acid. It is preferred to maintain the product of reaction in a neutral condition in order to simplify handling of it prior to its use. When it is to be used as a tanning agent it is acidified to a desired acid condition, for example to a pH of 3.5 with 33% sulfuric acid. The reaction product can be prepared at any concentration consistent with proper reaction.

Furthermore, a water solution of it can be evaporated to provide a dry, reddish brown powder which can be redissolved and used as a tannin.

It is important to maintain the amounts of the alkali metal salt of sulfurous acid and the aldehyde above certain minimum amounts relative to the yacca gum in order to obtain a water soluble reaction product which shows no turbidity upon being acidified to a pH of 2.5 and which provides proper tanning. It is important further to maintain the molar proportion of alkali metal salt of sulfurous acid to aldehyde at such values that the former is not in substantial excess of the latter.

The amount of the alkali metal salt of sulfurous acid can best be expressed in terms of its —SO_3, i. e. sulfite, content while the amount of aldehyde can best be stated in terms of the —CHO, i. e. aldehyde, contained in it. Thus, referring to the relative molar proportions of the ingredients, in a reaction batch the yacca gum content of which is one part, employing an —SO_3 charge of less than 2.5 parts or employing a —CHO charge of less than 5 parts and carrying out the reaction described above results in a product of reaction which precipitates from its water solution under acid conditions. Since the tanning procedure normally is carried out in acid solution such a precipitation is undesirable.

The preferred tanning agent of this invention is prepared by reacting, in the following relative molar proportions, one part of yacca gum with reagents containing 2.5 to 5.4 parts of —SO_3 and 5.0 to 11.2 parts of —CHO. It is important further that the —SO_3 be present in the reaction batch not in substantial excess on a molar basis over the —CHO. Raising the proportion of —SO_3 beyond its indicated upper limit without a corresponding increase in the proportion of the —CHO component, or employing a proportion of —SO_3 even below its upper limit but in substantial excess of the —CHO, results in a reaction product which evolves objectionable SO_2 fumes when it is acidified prior to tanning. This causes the solution to become astringent such that hides or skins treated in it shrink and shrivel. Furthermore, problems of air polution are created by the evolution of the SO_2 fumes. The presence of an undue excess of —CHO in the reaction batch over the —SO_3 component results in the production of a high molecular weight reaction product which is insoluble in water due to the size of its molecules. However, it is possible to increase the quantities of both the —SO_3 and —CHO above their indicated upper limits relative to the yacca gum, if they are added in substantially equimolar portions above their upper limits, without suffering the disadvantages stated above to result when either limit is exceeded alone. Such a joint, equimolar increase of the —SO_3 and —CHO contents merely causes further —CH_2SO_3Na groups to add to the yacca gum with the result that its water solubility is thereby even further increased. When the yacca gum is rendered excessively soluble by addition to it of too many —CH_2SO_3Na groups, it loses its effectiveness as a tanning agent, so that it is inefficient to increase the —SO_3 and —CHO contents beyond the amounts required to render the yacca gum soluble. However, a controlled increase in the proportions of —SO_3 and —CHO is within the spirit of this invention although not essential to its practice.

Solutions of water soluble tanning agents such as the reaction product of the present invention generally contain from ½% to 10% by weight of the tanning agent in water. This amount will vary according to the dictates of the individual tannery, however, with most tanneries varying the concentration of the agent even during the tannage of an individual hide or skin.

It is an important feature of this invention that the present tanning agent is water soluble even under strongly acid conditions, since tanning normally is carried out in an acid medium. Thus, it is possible and even preferred to employ this tanning agent at a pH of approximately 3.5. However, the preference of the individual tannery determines the particular pH used.

Skins or hides of animals generally used for making leather may be treated with the tanning agent of and according to the process of the present invention. In the specification the terms "hide" or "skin" are to be understood in their broad sense as including these materials. These terms are intended to include hides and skins in the condition in which they are normally employed for tanning treatment, e. g. in a bated or pickled state.

The skins or hides are immersed in the tanning bath which comprises a water solution of the tanning agent of the present invention held at the proper pH. Thus immersed they are subjected to a tanning treatment for a period depending upon the activity of the tanning agent and the thickness and denseness of the hide. Thereafter the hide generally is washed with water to remove excess tanning agent, salts, acids and the like.

The following example is given as of assistance to aid in understanding the invention but it is to be understood that the invention is not restricted to the reagents or conditions set forth in the example:

Example

31.7 gal of water, 88.3 lb. of finely divided yacca gum, and 61.8 lb. of anhydrous (98%) sodium sulfite were charged into a glass lined open reaction vessel provided with heating elements, a stirrer and a thermometer. These ingredients were stirred to effect a dispersion of the yacca gum and 46.8 lb. of 37% formaldehyde mixed with 10.6 gal. of water were added to them. The resulting reaction batch was then well mixed and heated at 70° C. for six hours. Reaction was discontinued at the end of this time, when a test sample taken from the reaction vessel and brought to room temperature showed no precipitation upon being lowered to a pH of 2.5 by addition of 33% sulfuric acid. Following the reaction the material was allowed to cool in the reaction vessel. The material at this point was in alkaline condition and 33% sulfuric acid was added to it with stirring until it was neutralized.

33% sulfuric acid was then added to the neutral solution of tanning agent obtained from the above reaction, until the solution reached a pH of 3.5. The acid solution was then diluted to a solids concentration of 4% and a bated calf hide was immersed in the diluted solution at room temperature for ten days. The hide was then removed from the solution, washed with water and dried. The hide was found to have been converted to a leather which was soft and full and was similar to a vegetable tanned leather. A sample of the leather was subjected to the conventional shrinkage test and showed no shrinkage at temperatures up to 80° C. After the shrinkage test the sample retained its flexibility and softness after drying.

Having described our invention, what we claim as new and desire to secure by Letters Patent of the United States is:

1. The herein described tanning agent obtained by reacting in aqueous medium an alkaline mixture containing one part, by molar proportion, of unmodified yacca gum, 5.0 to 11.2 parts of formaldehyde and 2.5 to 5.4 parts calculated as sulfite, of an alkali metal salt of sulfurous acid selected from the group consisting of alkali metal sulfites, alkali metal bisulfites, and alkali metal metabisulfites, the molar proportion of the sulfite not being in substantial excess of that of the formaldehyde, at temperatures of 70–110° C. until the product is soluble without precipitate in water acidified with sulfuric acid to a pH of about 2.5.

2. The herein described tanning agent obtained by reacting in aqueous medium a mixture containing one part, by molar proportion, of unmodified yacca gum, 5.0 to 11.2 parts of formaldehyde, and 2.5 to 5.4 parts of sodium sulfite, said sulfite not being present in substantial molar excess of the formaldehyde, at temperatures of 70–110°

C. until the product is soluble without precipitate in water acidified with sulfuric acid to about pH 2.5.

3. A tanning process which comprises the step of tanning hides and skins with a water solution of the tanning agent defined in claim 1.

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