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METHOD OF TANNING SKINS

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This invention relates to the tanning of skins and pelts for the purpose of producing a durable, water resisting leather which is light in color. The invention relates particularly to the tanning of skins by means of alum (aluminum sulfate) whereby light colored, water resistant skins can be economically produced.

Heretofore, mineral tanned skins have been tanned by means of various salts, such as salts of aluminum, iron, chromium, etc. It has been recognized that alum tanned skins are of considerably lighter color than those produced by chromium or iron. However, alum tanned skins are not water resistant and have certain other objectionable characteristics that interfere seriously with their general use in the manufacture of many finished leather products.

In view of the shortcomings of alum tannage, it has been customary, in order to produce light colored leather, to bleach chrome tanned skins. One common method of bleaching consists in the use of a syntan treatment that follows the chrome tanning treatment. In this way it has been possible to obtain a leather which resists water effectively and which is tolerably light in color for the purpose of light shades of leather. Nevertheless, the finished tanned products have certain disadvantages. In the first place, the material has a distinct bluish cast which can not be processed to produce a permanent white leather. The bleaching effect is limited to the surface of the skins. As a result, if the leather is worn or scuffed, the area exposed is of considerably darker tone than the remaining surface. Notwithstanding these and other objections, the trade has preferred chrome tannage for light colored leathers, as well as leather wherein the color is of no importance.

The chrome tanned skins are made in various ways, but in general the procedure involves subjecting pickled skins to the action of a soluble basic chromium sulfate which may be supplemented by the use of formaldehyde. The skins are then partly neutralized by the addition of sodium bicarbonate in order to reduce the amount of free sulfuric acid which has been produced by the tannage treatment. The neutralization is restricted to maintain a sufficiently low pH to assure complete solubility of the spent chrome liquors. Subsequently the skins are washed, bleached (if this operation is necessary for the particular quality of skin desired) and finally fat liquored. The fat liquoring operation almost invariably consists in treating the skins with a soap or a sulfonated oil in which there may be dispersed an unsulfonated oil.

It has been proposed heretofore to substitute alum (aluminum sulfate) for chromium sulfate and otherwise proceed as in the chrome tannage treatment. However, such procedures have met with little or no commercial success, due to the fact that the alum in the skins is not resistant toward water and may, in fact, be leached out in substantial quantities by merely immersing the skins in water. In this respect the alum tannage differs radically from chrome tannage.

I have now found that if the alum tannage is followed by a treatment with a suitable base, the aluminum is thereby combined or fixed with the skins whereby it cannot be leached out by means of water as is true of the alum tannage. The amount of base which is necessary for this fixation is substantially greater than that which has been used heretofore to partially neutralize the acidity developed during the tannage. As a matter of fact, the amount of base necessary is at least sufficient to develop a pH high enough to precipitate the alum which remains in the spent aqueous solution. The degree of neutralization which is preferred, according to my process, is well in excess of that which develops puckering or drawing of the grain of the leather, and the neutralized skins produced by my treatment are in this respect inferior to skins which are neutralized only as required by prior practice. Nevertheless, it is to be noted that this neutralization is necessary in order to assure adequate fixation of aluminum and consequent water resistance. Moreover, I have found that the phenomenon of drawn grained leather can be remedied or obviated according to one of the features of my invention by means of the syntans, such as are sold in commerce. In general any of the syntans are satisfactory, especially the sulfonated sulfones, aromatic hydrocarbons and phenols, which sulfonated materials are polymerized with formaldehyde. When a specially light colored leather is required, it is desirable to select a syntan which is stable to light, although I have found that whether the syntan is stable to light or not, it functions effectively to overcome or remedy the drawing of the grain of the leather.

The leather so produced will be found to be of excellent tanned quality and is then ready for fat liquoring. I have found that when one proceeds to this stage of my improved tanning process, one obtains a leather which would appear to anyone skilled in this art to be of well tanned quality.

Strangely enough, however, when one proceeds with the conventional fat liquoring operation which involves the use of sulfonated oils one immediately obtains a skin which is extremely sticky and practically impossible to wash. The resulting product is wholly unsatisfactory for use in the art.

However, I have found that whereas the sulfonated type of fat liquors are wholly unsatisfactory in practicing my invention, one can obtain a leather of excellent quality which is well fat liquored if one substitutes for the sulfonated type of fat liquors a neutral fat liquor. For this purpose a fat liquor which is essentially a mixture of neat's foot oil dispersed in an aqueous medium by means of a neutral dispersing agent, as for example, egg yolk, lecithin and the like, will be found to give excellent results. The addition of flour and clay or other pigments to the fat liquoring solutions as is now commonly practiced may be included advantageously.

Various modifications to the procedure outlined above may be employed. Thus, for example, the addition of formaldehyde to the alum tannage is advantageous. I have also found that instead of adding the syntan to the leather after the grain has been drawn by reason of neutralization, one can add the syntan to the alum treated skins and neutralize in the presence of the syntan, whereby the ill effect of neutralization is obviated.

The following examples are set forth to illustrate specific embodiments of the principles of my invention:

Example 1.—Hides or pelts are dehaired, bated, and pickled in the usual manner. For the purpose of the last operation the skins may be subjected for a period from four to eight hours to the action of an aqueous solution of sulfuric acid and sodium chloride, prepared by dissolving approximately ½ to 1 per cent of H_2SO_4 and from 10 to 12 per cent of sodium chloride in water. Approximately four pounds of this solution is used per pound of bated hide weight. After the pickling operation the skins are usually drained for 24 to 48 hours.

Before undertaking the mineral tanning steps, it is advantageous to mill the drained hides for 10 minutes with an equal weight of 4 per cent aqueous sodium chloride solution. Moreover, the skins usually retain considerable absorbed acid which should be neutralized in part, preferably by the addition of a mild base. To this end one may add approximately 10 per cent of the weight of the drained skins of hypo crystals ($Na_2S_2O_3.5H_2O$). After milling the stock in this solution for about twenty minutes, it is ready to be processed according to principles of my invention. It is to be understood, of course, that the foregoing steps are not in and of themselves new and that the procedure up to this point may be varied in various ways as is well-known in the art.

The alum tannage is effected by adding to the neutralized mixture approximately 20 per cent by weight of the drained skins of iron free alum of commerce. At the end of approximately one hour I prefer to add a formalin solution to the mixture to supplement the mineral tannage. For this purpose I add approximately 2 per cent of formalin (40 per cent aqueous formaldehyde) based on the weight of the drained skins and continue to mill the skins for about 4 hours.

The skins treated in this manner hold the aluminum in relatively loose combination which can be removed by prolonged leaching with water. To fix the aluminum permanently it is necessary to reduce the acidity of the original skins, as well as the acidity developed in the tannage treatment. For this purpose I add slowly to the mill, approximately 7½ per cent of sodium bicarbonate, based on the weight of the drained skins (referred to above, immediately following the pickling operation). After all of the base has been added, the skins are milled for approximately 3 hours to complete the neutralization and fixation of the aluminum, whereupon they are removed from the mill, drained and horsed up for 24 hours. The water in the horsed skins is subsequently wrung out after which the skins are split and shaved in the usual manner.

It is to be noted that the amount of sodium bicarbonate (or other base) which is added, is more than sufficient to precipitate the aluminum salt which is in water solution and thereby produce a liquor which is not optically clear. In this respect my process differs from the conventional alum or chrome tannage processes. It is also to be noted that other bases may be added in lieu of the bicarbonate such, for example, as soda ash. In either case the skins become puckery and develop a drawn grain; a manifestation which is considered highly objectionable from the tanner's point of view.

According to my invention, to overcome the objection of a puckered skin having a drawn grain, the skins are subjected to the action of a syntan. Most of the syntans of commerce are formaldehyde condensation products of aromatic sulfonic acids, or aldehyde condensation products of sulfonated sulfones or phenols. I prefer to use the products of high quality which are relatively stable to light, especially if the finished product is to be used in white leather.

The syntan treatment involves simply placing the split-shaved skins into a mill with an equal weight of water, adding 10 per cent (of the weight of the skins) of commercial aqueous syntan and milling for about one and a half to two hours, after which the skins are drained and horsed up for 24 hours, preparatory for the fat liquoring operation.

The skins thus obtained will be found to have regained a smooth grain and will otherwise be found to be of excellent quality.

Example 2.—Proceed as in Example 1 up to and including the four-hour milling operation in the presence of the formalin. Subsequently add approximately 7½ per cent of a commercial syntan (based on the weight of the skins) to the drum containing the hides and mill for 1½ to 2 hours. Thereafter drain the skins, replace the drained liquor with a quantity of water equal to the volume of the drained liquor and add slowly about 7½ per cent of bicarbonate of soda, as in the foregoing example. After all of the bicarbonate has been added, the skins are milled for about 3 hours to complete the neutralization.

The neutralized skins are then horsed up, split, shaved in the usual manner, and finally worked and fat liquored.

Example 3.—One hundred pounds of bated stock are introduced into a paddle mill or drum with an equal weight of water in which is dissolved 5 per cent of ordinary salt and ½ per cent of sulfuric acid. After thoroughly milling the skins in this pickling mixture for a few minutes, there is added an amount of commercial iron free alum (aluminum sulfate) equivalent to approximately 20 per cent of the weight of the skins.

This mixture is then milled for 1 hour, after which there is added about 2 per cent of formalin as described in the foregoing examples, and the hides are subsequently milled for an additional period of about 4 hours. These hides are then ready for neutralization followed by syntan treatment, as described in Example 1, or the alternative treatment with the syntan followed by neutralization as described in Example 2.

Example 4.—If the skins produced according to Examples 1, 2, or 3 are subjected to a conventional fat liquoring operation, the product obtained would be practically worthless, since it forms a sticky, pasty mass on the surface of the leather. However, I have found that instead of using a soap or a sulfonated type fat liquor, one may obtain excellent results by means of neutral fat liquors, such as are obtained by dispersing the usual oils, for example, neat's-foot oil, in an aqueous solution containing a dispersing agent that is itself free of sulfonic acid. Materials of this type are well known on the market and include egg yolk, lecithin and others.

For the purpose of my invention the skins which have been treated with a syntan and have subsequently been horsed up for 24 hours, are washed and thereafter treated with a neutral fat liquor. The fat liquor is made by mixing with sufficient water to form a paste: 5 parts of dry egg yolk (or 12.5 parts of liquid egg yolk) with 20 parts of raw neat's foot oil, 30 parts of flour, and 25 parts of fine colloidal clay. The paste is then dispersed in additional water to be able to fat liquor the skins effectively. The foregoing amount of fat liquor is sufficient to treat 700 to 1000 parts of drained tanned skins obtained by the foregoing examples. It is to be understood that other pigments may be added or substituted for the clay, such as titanium oxide, lithopone and the like; and, further, that the flour may be omitted if desired, although I prefer to use it.

The present invention is not limited to any specific neutralizing agent, moreover, neutral dispersing agents other than egg yolk, such as lecithin, gum tragacanth and the like, may be employed and, finally, the amount of the fat liquor, as well as the relative proportions of the constituents, may be varied according to the type of skin being treated and the quality which is being sought in the finished skins.

It is to be understood that inasmuch as sulfonated oils and soaps form reaction products which render the skins unfit for the intended purpose, their presence in fat liquor is objectionable, and for this reason I prefer that the fat liquor should be substantially free of sulfonated oils, soaps and, insofar as possible, free of fatty acids.

The syntans which I ordinarily use, and which are contemplated in the foregoing examples, are the light fast syntans of commerce which are sold as aqueous solutions containing approximately 30% solids of which about half is active organic tanning principle. The material is a sulfonic acid which is partly neutralized and contains practically no free sulfuric acid.

It is to be understood that one may substitute the evaporated or dried syntan. As indicated above, the neutralizing agent may be added to the syntan and the resulting mixture may be used in my process.

It is to be understood that the foregoing examples are illustrative, rather than limitative, of the principles of my invention, and that these principles are susceptible to variations and modifications without departing from their spirit.

What I claim is:

1. In the tanning of skins by the alum tanning process, the improvement characterized in that the skins which have been subjected to alum tannage are neutralized with sufficient base to precipitate aluminum salts from their aqueous solution and further characterized in that the drawn grain or puckery skin effect, which would otherwise impair the quality of the skin, is obviated in the finished product by treating the skins with a syntan either before or after neutralization.

2. In the tanning of skins by means of alum to produce leather which is light in color and resistant to water, the steps which include subjecting the skins to an alum tannage, subsequently treating the skins with a syntan and fixing the aluminum in the skin by neutralizing the alum tannage with sufficient base to precipitate aluminum salts from their aqueous solution, whereby the aluminum is no longer readily leached from the skins with water and thereafter fat liquoring the skins by means of a neutral fat liquor which is substantially free of sulfonated oil and of soap.

3. The method as defined in claim 2 and further characterized in that the fat liquor consists essentially of a neutral dispersing agent for the neat's foot oil in water and a pigment.

4. The method as defined in claim 2 and further characterized in that the fat liquor consists of a known softening oil for the leather, such as neat's foot oil, a materal for dispersing the oil in an aqueous medium which is substantially neutral and free from sulfonated oils, such as egg yolk, lecithin and the like, and a pigment such as clay and titanium oxide.

5. The method as defined in claim 2 and further characterized in that the fat liquor consists of a known softening oil for the leather, such as neat's foot oil, a material for dispersing the oil in an aqueous medium which is substantially neutral and free from sulfonated oils and soaps, such as egg yolk, lecithin and the like, flour, and a pigment such as clay and titanium oxide.

6. The improvement in the art of alum tannage characterized in that the aluminum is fixed on the skin by reducing the acidity to a point which, in the absence of a syntan, would not only produce a puckery skin having a drawn grain, but would precipitate aqueous solutions of aluminum salts.

7. In the tanning of skins by means of alum to produce leather which is light in color and resistant to water, the steps which include subjecting the skins to an alum and formaline tannage, subsequently treating the skins with a syntan and fixing the aluminum in the skin by neutralization with sufficient base to precipitate alum salts from the aqueous solution, whereby the aluminum is no longer readily leached from the skins with water and thereafter fat liquoring the skins by means of a neutral fat liquor which is substantially free of sulfonated oil and of soap.

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