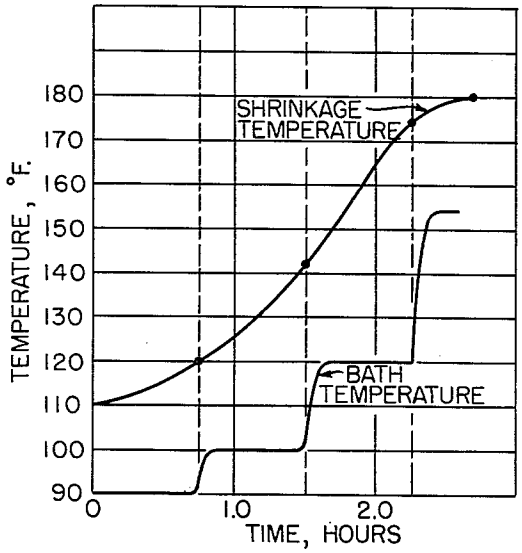
Oct. 31, 1961 A. E. USHAKOFF 3,006,714

TREATMENT OF ANIMAL SKINS

Filed Oct. 1, 1956

Fig. 1



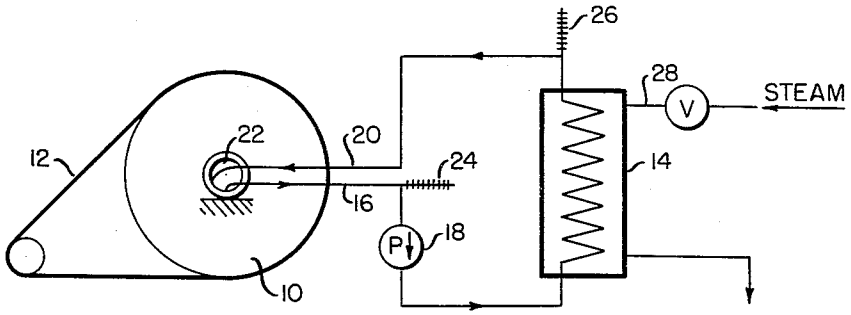


Fig. 2

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United States Patent Office 3,006,714 Patented Oct. 31, 1961

3,006,714
TREATMENT OF ANIMAL SKINS

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Filed Oct. 1, 1956, Ser. No. 613,338
10 Claims. (Cl. 8—94.18)

This invention relates to the treatment of animal skins and in particular to processes in which the water content of wet skins is extracted and replaced by a water-miscible organic solvent. The objects of the invention are primarily to render the skin of uniformly high permeability so that the solvent may readily and evenly penetrate the skin structure, and to so alter the relationship between the skin protein and the water associated with it that the amount of solvent required for dehydration is greatly reduced. A further object of the invention is to increase the resistance of the skin to the swelling or shrinking effects of acids or bases in solutions and which the skin is treated.

Advantageous use of the process of this invention may be made in conjunction with the process of forming hollow leather articles disclosed in Patent No. 2,582,298; with the processes of adjusting and fixing the texture of a skin disclosed in the copending application of the present inventor, Serial No. 263,129, filed December 24, 1951, now U.S. Patent No. 2,781,241; and with the processes of extracting the water from a skin by forcing a water-miscible organic liquid through it while it is supported on a flat porous bed disclosed in the copending application of the present inventor, Serial No. 233,924, filed June 27, 1951, now Patent No. 2,702,229.

In such processes, non-uniformity in the permeability of the skin leads to more rapid penetration and dehydration by the extracting solvent in the regions of high permeability, and the skin in the solvent dehydrated condition is far more permeable than when it is wet with water. Thus, a difficulty frequently encountered in solvent dehydration processes, especially those where the solvent is forced through the skin, is the selective extraction of the water from the more permeable regions followed by the channeling of substantially all the solvent subsequently applied to the skin through those initially dehydrated regions.

The present invention provides a pretreatment that successfully eliminates this difficulty, and at the same time reduces the amount of solvent required for dehydration. In general, the process of this invention consists in a treatment of the skin in an aqueous solution of formaldehyde at a temperature below the shrinkage temperature of the skin. The treatment is continued until the shrinkage temperature of the skin has raised substantially, during which time the bath temperature may be raised to accelerate the process. After the treatment, the skin has the general appearance of an untanned skin, but will be found to have a uniformly high permeability such that solvent dehydration will proceed without serious selective extraction of the water and will require less solvent. More over, when the skin has been pretreated its acidity or basicity may be varied considerably, yet without the swelling or shrinking that normally occurs with such changes. In this respect, the pretreatment process of this invention is effective to fix the texture of the skin in its condition existing during the pretreating process.

During the pretreatment process the bath should have a pH such that the pH in the skin is generally between about 2 and 5, preferably between about 3 and 4.5, and should contain formaldehyde in an amount of at least

about 0.5 percent of the wet weight of the skin. It is also desirable to include in the bath a reagent, such as salt, that prevents undue swelling of the skin, and in the low pH range the presence of salt has the desirable effect of causing the shrinkage temperature to increase beyond the maximum point that can be reached without the salt. Preferably, therefore, the bath contains about 2 percent by weight or more of dissolved salt.

In carrying out the pretreatment process, the skin is brought in contact with, and preferably immersed and drummed or tumbled in, the formaldehyde solution, and is maintained in contact with the solution until its shrinkage temperature has been raised to above about 155° F., preferably to above 170° F. The skin is then removed, and may be rinsed with water and further processed to extract and replace the water with a water-miscible organic solvent.

The preferred manner of practicing this invention consists in drumming the wet skin in an aqueous bath having a pH between about 3 and 4.5, a formaldehyde concentration of at least about two percent by weight, and a salt content of about four percent by weight, while raising the temperature of the bath as the shrinkage temperature increases to maintain the bath temperature below the shrinkage temperature of the skin by at least about 20 Fahrenheit degrees. The temperature of the bath is accordingly preferably raised to at least about 135° F., without however exceeding the shrinkage temperature of the skin. Under these conditions, the skin may be fully pretreated in about two hours. By maintaining the bath temperature fewer degrees below the shrinkage temperature, the time required may be decreased; and conversely a greater temperature differential prolongs the time required to raise the shrinkage temperature the desired amount. The process may be carried out at room temperature, but requires a considerably longer period of time, generally 24–48 hours, before the shrinkage temperature has reached the desired value.

At the low pH level at which the skins are preferably treated, it has been found that salt in the bath is desirable in assisting the continued increase of the shrinkage temperature above about 150° F. Thus the salt may be omitted until the shrinkage temperature has reached about 150° F., but it is desirably present throughout since it prevents unnecessary swelling of the skin.

Under the preferred conditions outlined above, the shrinkage temperature of the skin is brought to between about 155° F. and 190° F., a shrinkage temperature generally lower than that of a fully tanned skin. A shrinkage temperature above 190° F. is not generally attained with formaldehyde under the preferred conditions of treatment. The process may however be carried out in the presence of additional tanning agents, added either along with the formaldehyde or subsequently to the pretreatment process, in which case the shrinkage temperature may well reach a much higher figure.

It is, of course, necessary in controlling the process to determine the shrinkage temperature of the skin from time to time. This may be done by immersing a strip of the skin in cold water under a slight spring tension, then heating the water, while stirring, at a rate of 3–5° C./min. until the skin begins to shrink, at which point the shrinkage temperature may be noted.

This invention will be more fully appreciated from the following description of the best manner yet devised for carrying it out. Reference is made to the drawings in which:

FIG. 1 is a graph showing the rise in the shrinkage temperature of the skin and the manner in which the

temperature of the bath is raised during a typical pretreatment process, and

FIG. 2 is a diagrammatic representation of one apparatus for carrying out the process.

In carrying out the process of this invention in the apparatus shown in FIG. 2, a wet pickled skin is placed in a drum **10**, mounted for rotation on a horizontal axis and driven through a belt **12** by any convenient means. The treating solution is circulated between the drum and a steam heated heat exchanger **14** through an effluent line **16**, in which is a pump **18**, and an influent line **20**, both of which enter the drum through a hollow supporting trunnion **22**. Thermometers **24** and **26** are situated in each of the lines to indicate the temperature of both the outgoing and incoming solution. The heat exchanger **14** is fed by steam through a valved line **28**, and condensate is drained off through a condensate conduit **30**.

EXAMPLE I

In a typical operation a wet pickled skin weighing about 16,000 grams was placed in the drum which contained 5 gallons of treating solution consisting of

	Parts by weight
Formaldehyde (aqueous, 40%)	5
Salt (NaCl)	4

Sulfuric acid—to adjust the pH to 3.8.
Water—to make up 100 parts by weight.

The shrinkage temperature of the skin was determined initially and at 45 minute intervals, and at each determination the bath temperature was brought to a temperature about 20 Fahrenheit degrees below the shrinkage temperature, and held there. The temperature of the bath was controlled by circulating the bath continuously between the drum **10** and the heat exchanger **14** while admitting steam to the exchanger through the line **28** as required to maintain the desired temperature. The operating conditions are reported in Table I and shown in the graph of FIG. 1.

Table I

Time	Shrinkage Temp., ° F.	Bath Temp., ° F.
0	110	90
45 min	120	100
90 min	143	120
135 min	175	155
150 min	180	155

When the shrinkage temperature had reached 180° F., the skin was removed and washed with water. It was then dehydrated by forcing acetone through it while supported on a flat porous bed, as disclosed in application Serial No. 233,924, now Patent No. 2,702,229, referred to above. For comparative purposes a sample from the same skin, pickled but not pretreated, was also dehydrated in the same manner. In each case, the acetone was forced through the skin until the specific gravity of the effluent acetone had fallen to 0.810 (20° C.), corresponding to a water content in the acetone of about 7 percent by weight.

The untreated skin was found to have been only partially dehydrated in certain regions, or islands, which were still noticeably wet with water. The pretreated skin, on the other hand, was completely permeated by the acetone, and no regions of incomplete dehydration were found. Moreover, the pretreated skin required only 60% of the acetone required for the pickled skin for that degree of dehydration represented by a specific gravity for the acetone of 0.810.

It will be understood that the process described above may be accelerated considerably by maintaining the 20-degree temperature differential more closely, but this requires more frequent checking of the shrinkage temperature of the skin. The process also proceeds more rapidly if a smaller temperature differential is maintained, but 20 degrees is considered a safe minimum if the danger of shrinking the skin by exceeding its shrinkage temperature is to be avoided entirely. The determination of shrinkage temperature is generally not so precise that the skin may be held for prolonged periods at any point just below the determined shrinkage temperature. In this connection, however, skins have been pretreated in accordance with this invention by heating the bath at a uniform rate of temperature rise from 90° F. to 160° F. in one hour. At the end of the run the skin was found to be completely pretreated with a shrinkage temperature of 165° F. It has been found that an effect of increasing the temperature of the pretreating bath is a corresponding acceleration in the reaction rate which makes it possible, under the preferred conditions, to bring the bath up to its final temperature, e.g. 135° F., very rapidly. The increase in temperature of the bath from a starting temperature of 90° F. to a final temperature of 135° F. may be carried out while drumming the skin in a period of time of about 10 minutes. A rapid treatment is particularly preferred where it is desired that the skin be as limp, flexible and stretchy as possible.

In the embodiment described above, the formaldehyde was present in a concentration of about 2.0% by weight. In the amount of treating solution present this was considerably in excess of the minimum amount necessary, 0.5% on the wet weight of the skin, but a concentration about that high, or higher, is desired in order that the reaction may proceed at a desirably rapid rate. Lower formaldehyde concentrations may be used, but the process proceeds at a slower rate, and the time allowed for it must be correspondingly increased.

EXAMPLE II

In treating large batches of pickled skins, the acidity of the skin may be utilized to maintain the desired pH conditions. In general, the wet pickled skins, having a pH of about 3–3.5, are tumbled in the formaldehyde solution while the solution is heated as the shrinkage temperature rises.

In a typical procedure, pickled skins having a pH of about 3–3.5 are placed in the drum to which is added about 5 percent based on the wet weight of the skins of a commercial 40% formaldehyde solution. To provide a volume of solution in the drum sufficient for thorough treatment of the skins, additional solution may be necessary, in which case there is added a mixture consisting of:

	Parts by weight
Formaldehyde (40%)	7.5
Salt (NaCl)	4
Water	100

in the amount necessary for proper drumming of the skins. Additional acid is also added if necessary to maintain the pH at about 3–3.5.

The added solution, it is noted, is of about the same composition as the combination of the formaldehyde originally added and the water in the pickled skins, which generally represents about ⅔ of their weight, and thus its addition does not alter the equilibrium formaldehyde concentration of the treating solution in the drum.

Table II

Time, minutes:	Temperature, ° F.
0	80
15	110
30	130
45	140
60	150

The skins are then drummed while the temperature of the bath is raised, for instance from an original temperature of 80° F. to a final temperature of 150° F. according to the time-temperature pattern shown in Table II. At the end of the treatment the shrinkage temperature of the skins is about 180° F.

The skins are thereafter removed and rinsed of excess treating solution and are ready for solvent dehydration. The treating solution remaining is advantageously fortified by the addition of formaldehyde, salt and water as required to bring it to its original composition, preliminary to the treating of additional skins.

In the pretreatment process the skin absorbs formaldehyde in an amount depending on the pH but generally about 0.5 percent of its dry weight. The manner by which formaldehyde raises the shrinkage temperature and increases the permeability of the skin is not completely understood, but it is believed that the effect of the pretreatment is to remove water bound up with the fibers of skin substance, yet without changing the total water content of the skin, for no such change has been observed.

Although the invention has been described with specific reference to formaldehyde as the pretreating reagent, it will be understood that other reagents are equivalent thereto and are equally effective, particularly paraformaldehyde, and hexamethylene tetramine. It is also to be noted that the solvent dehydration step for which the skins have been specially conditioned, need not follow immediately after the pretreatment operations. The pretreatment may be followed by tanning or other processing steps, following which the skins are solvent, dehydrated and dried. In fact, if the skin is to be tanned, treatment with aqueous solutions of the tanning agent is preferably carried out after the pretreatment, with solvent dehydration following the tanning treatment.

Upon dehydration by extraction of the water with a water miscible organic solvent, the skin acquires the feel and appearance of a tanned skin, and the solvent may be evaporated from the skin without causing the skin to harden or stiffen. The dried skin may, however, be readily rewet with water and is then semi-plastic and of the feel and appearance of an ordinary untanned wet skin. By dehydrating and drying a skin in this manner, untanned skins may be shipped dry to the tanner, and there rewet and tanned in the ordinary manner.

Although for best results the pH should be in the range of 2–5 during the pretreatment process, higher pH conditions up to a pH of about 9 may be used but with diminishing benefit to the permeability of the skin.

This application is a continuation-in-part of applicant's copending application, Serial No. 481,999 filed January 17, 1955, which in turn is a continuation-in-part of application, Serial No. 330,067 filed January 7, 1953, both now abandoned. The results of further work carried out since the filing of the parent case are presented herein in order that the invention may be more fully appreciated and more precisely defined.

Having thus disclosed my invention and described in detail the preferred embodiment thereof, I claim and desire to secure by Letters Patent:

1. In the process of extracting and replacing water in water-wet untanned animal skin by treating said skin with an inert water miscible organic solvent, the method of increasing and rendering uniform the permeability of the skin to the solvent comprising contacting said skin with an aqueous bath containing at least about 0.5 percent of formaldehyde based on the weight of the wet skin at least until the shrinkage temperature of the skin has reached 155° F., while maintaining said bath at a temperature below the shrinkage temperature of the skin and at a pH such that the pH in the skin is between about 2 and 9, then contacting said skin with a liquid consisting essentially of said inert water-miscible organic solvent until the water in the skin is extracted and replaced by solvent.

2. In the process of extracting and replacing water in water-wet untanned animal skin by treating said skin with an inert water miscible organic solvent, the method of increasing and rendering uniform the permeability of the skin to the solvent comprising contacting said skin with an aqueous bath containing at least about 0.5 percent of formaldehyde based on the weight of the wet skin at least until the shrinkage temperature of the skin has reached 155° F., while heating the skin and bath to bring the temperature to 135° F. in less than about 2 hours and maintaining said bath at a temperature below the shrinkage temperature of the skin and at a pH such that the pH in the skin is between about 2 and 9, then forcing a liquid consisting essentially of said inert water-miscible organic solvent through said skin until water in the skin is replaced with said solvent.

3. In the process of extracting and replacing water in water-wet untanned animal skin by treating said skin with an inert water miscible organic solvent, the method of increasing and rendering uniform the permeability of the skin to the solvent comprising contacting said skin with an aqueous bath containing at least about 0.5 percent of formaldehyde based on the weight of the wet skin at least until the shrinkage temperature of the skin has reached 155° F., while maintaining said bath at a temperature below the shrinkage temperature of the skin and at a pH such that the pH in the skin is between about 2 and 5, then contacting said skin with a liquid consisting essentially of said inert water-miscible organic solvent until the water in the skin is extracted and replaced by solvent.

4. The process defined by claim 3 wherein the skin is treated with the inert water-miscible organic solvent by forcing the solvent through the skin.

5. In the process of extracting and replacing water in water-wet untanned animal skin by treating said skin with an inert water miscible organic solvent, the method of increasing and rendering uniform the permeability of the skin to the solvent comprising contacting said skin with an aqueous bath containing at least about 0.5 percent of formaldehyde based on the weight of the wet skin at least until the shrinkage temperature of the skin has reached 155° F., while heating the skin and bath to bring the temperature to 135° F. in less than about 2 hours and maintaining said bath at a temperature below the shrinkage temperature of the skin and at a pH such that the pH in the skin is between about 2 and 5, then contacting said skin with a liquid consisting essentially of said inert water-miscible organic solvent until water in the skin is replaced with said solvent.

6. The process defined by claim 5 wherein the skin is treated with the inert water-miscible organic solvent by forcing the solvent through the skin.

7. In the process of extracting and replacing water in a water-wet untanned animal skin by treating said skin with an inert water miscible organic solvent, the method of increasing and rendering uniform the permeability of the skin to the solvent comprising contacting the skin with an aqueous bath containing at least about 0.5 percent formaldehyde based on the weight of the wet skin and at least about 2 percent of dissolved salt which prevents undue swelling of the skin, based on the weight of the bath, at least until the shrinkage temperature of the skin has reached 155° F., while maintaining said bath at a temperature below the shrinkage temperature of the skin and at a pH such that the pH in the skin is between about 2 and 5, then forcing a liquid consisting essentially of said inert water-miscible organic solvent through said skin until the water in the skin is replaced with said solvent.

8. In the process of extracting and replacing water in water-wet untanned animal skin by treating said skin with an inert water miscible organic solvent, the method of increasing and rendering uniform the permeability of the skin to the solvent comprising contacting said skin with an aqueous bath containing at least about 0.5 percent of formaldehyde based on the weight of the wet skin and at least about 2 percent of dissolved salt which prevents undue swelling of the skin, based on the weight of the bath, at least until the shrinkage temperature of the

skin has reached 155° F., while heating the skin and bath to bring the temperature to 135° F. in less than about 2 hours and maintaining said bath at a temperature below the shrinkage temperature of the skin and at a pH such that the pH in the skin is between about 2 and 5, then forcing a liquid consisting essentially of said inert water-miscible organic solvent through said skin until water in the skin is replaced with said solvent.

9. In the process of extracting and replacing water in water-wet untanned animal skin by treating said skin with an inert water miscible organic solvent, the method of increasing and rendering uniform the permeability of the skin to the solvent comprising contacting said skin with an aqueous bath containing at least about 2 percent of formaldehyde based on the weight of the bath and at least about 4 percent of dissolved salt which prevents undue swelling of the skin, based on the weight of the bath, at least until the shrinkage temperature of the skin has reached 155° F., while heating the skin and bath to bring the temperature to 135° F. in less than about 2 hours and maintaining said bath at a temperature below the shrinkage temperature of the skin and at a pH such that the pH in the skin is between about 2 and 5, then forcing a liquid consisting essentially of said inert water-miscible organic solvent through said skin until water in the skin is replaced with said solvent.

10. The process defined by claim 9 wherein the inert organic solvent is acetone.

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