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TANNING IN A NONAQUEOUS MEDIUM

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My invention relates to the treatment of hides and skins.

In the well-known chrome tanning process, a skin or hide pretreated to remove hair and treated by various other steps such as bating and pickling, is immersed for an extended period in a solution of basic chromium sulphate. Ordinarily this chromium treatment of the skin or hide is carried on in a "paddle" or a drum during the chrome treating period and is then removed from the "paddle" or drum and aged for a period of from several hours up to two days.

In the vegetable tanning process, dehaired and otherwise pretreated skins or hides are subjected to various steps including a prolonged soaking treatment in a solution containing various vegetable extracts. Tanning by the vegetable method occupies a period of several weeks and involves extensive handling of the hides.

By either of these common methods of tanning, extended periods of time are required so that to insure continuous production of leather a very large number of skins or hides must be maintained in various stages of tanning. Investment in skins or hides and in treating tanks, vats, or other treating equipment is large so that the cost of the ultimate leather is high.

It is an important feature of my invention to convert skin and hide material to a stable nonputrescible leatherlike condition by a short and simple treatment of the skin or hide materials with a new type of reagent. By my new process there is formed a tough, pliable product similar to leather in appearance and in many other properties. The new product will withstand prolonged soaking in water without marked shriveling or hardening even at relatively high temperatures, and is exceptionally resistant to mold growth.

I have discovered that skins or hides may be converted to this novel leather-like material by drying the skin or hide material and contacting the dried material with certain acid chlorides. These acid chlorides are ordinarily employed in the form of solutions which readily penetrate the skin or hide. I have made the further discovery that a product possessing increased softness and flexibility and an improved appearance is formed where certain special solvents are employed in combination with the active treating agents.

For treatment according to the process of the present invention, I have found that bated or pickled skins or hides, for example calf-skins or steer hides, are satisfactory. Skins or hides in

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other conditions may also be used. For most satisfactory treatment, the hide or skin should have a pH of between about 5 and about 7 prior to treatment. However, skins or hides having a pH somewhat outside these approximate limits may be treated.

Skins or hides of animals generally used for making leather may be treated according to the process of the present invention. In the specification the term "skin" or "skin material" are to be understood in their broad sense as including these materials. The term "hide" in the claims is intended to include both skins and hides in the condition in which they are normally employed for tanning treatment.

Where a pickled material is used, it is first subjected to a conventional depickling operation. The depickled skin is then immersed in water with agitation to remove dissolved salts and other soluble materials. A suitable treatment period may range from around two hours for calfskin to four hours for a steer skin.

The depickled and soaked skin is then dried to a moisture content which may be between about 10 and about 15%. This moisture content is determined by comparison with the weight of the skin when subjected to a further drying for sixteen hours in air at 105° C. It has been found that drying is most satisfactorily accomplished by the action of solvents, for example, acetone, methyl acetate, isopropyl alcohol, dioxane, methyl Cellosolve acetate or other solvent which will remove the water without seriously harming the skin. This drying may be effected by leaving the skin immersed in an agitated bath of the solvent overnight. The solvent is then removed from the skin, suitably by evaporation in a stream of dry, warm air.

The above is but one of many conceivable methods for treatment of a skin prior to the treatment with my new agents. Modifications will be readily apparent to persons familiar with the handling of skins. For example, a bated skin need not be subject to the depickling and washing operations above outlined.

The dried skin is immersed in a body of the liquid treating agent and is maintained in the liquid for a sufficient period to convert the skin to the new leather-like condition.

I have found that the acid chlorides of aliphatic hydrocarbons or their derivatives having from 3 to 18 carbon atoms are very effective treating agents. Among compounds in this class are propionyl chloride, butyryl chloride, heptoyl

chloride, pelargonyl chloride, lauroyl chloride and stearoyl chloride. Di-acid chlorides of dicarboxylic acids having at least four carbon atoms have also been found effective to convert skin and hide material to leather-like condition. Among these agents are succinyl chloride, fumaryl chloride, adipyl chloride, sebacyl chloride, phthalyl chloride, and diglycollyl chloride. Also, m-sulphobenzoyl di-chloride and phenoxy acetyl chloride have been used in the treatment of skin and hide materials to form desirable leather-like products.

Still further acid chlorides which do not fall within any of the above groups are trichloracetyl chloride and chloracetyl chloride.

These treating agents are ordinarily employed as solutions in organic solvents in order that they may penetrate well into the interior of the skin material, and in order to avoid a too vigorous reaction between the material and the treating agent. Methyl "Carbitol" formal, the formal of the monomethyl ether of diethylene glycol, has been found particularly satisfactory as a solvent for the treating agent, and solutions comprising it give particularly soft and fine-appearing, leather-like products. Methyl "Cellosolve" formal, the formal of the monomethyl ether of ethylene glycol, has also been used as solvent with many of applicant's treating agents, and the solutions have been found to give very desirable products. A preferred range of concentrations of solutions is from about 10% to about 50% treating agent by volume based on the volume of the solution.

The time of immersion of the skin in the treating agent varies with the weight and type of skin treated. Preferred times of treatment may be from about one-half hour to about five hours. In the case of a calfskin, satisfactory action has been obtained by immersion of the prepared, dried, calfskin for about two hours at about 130° F. temperature in a 50% solution of adipyl chloride in methyl "Carbitol" formal. In the case of steer hide, a five hour immersion in the same solution at 130° F. has been found satisfactory.

Comparable effects on these materials have been obtained with a treating time of three hours, using as treating agent a 50% solution of pelargonyl chloride in methyl "Cellosolve" formal at 110° F. temperature.

As illustrated above, the temperature of the treating bath may vary. Factors controlling the temperature include the boiling points and vapor pressure of the solvents and of the treating agents and the rate of treating action desired.

After the above treatment, the skin is removed from the treating bath and is immersed in a solvent to remove soluble materials such as excess agent, reaction products and the like. Suitable solvents for this use are tri-chlorethylene, acetone and toluene.

The skin is removed from the solvent bath and is permitted to dry. The dried skin is then placed in a neutralizing bath, which may be a depickling solution, until it reaches a pH of about 7 or other value depending upon the properties desired. This step is desirable in that it also serves to neutralize or decompose acid compounds which may have formed within the skin. The skin is finally washed to remove salts, and is then removed from the washing bath.

The treated skin may be subjected to such further treatments as desired, for example, dyeing, fat liquoring or stuffing, drying and surface finishing.

The following examples are given as illustrative of processes in accordance with the present invention. It is to be understood that the invention is not restricted to the reagents and procedural details disclosed in these examples.

Example 1.—A pickled calf-skin was depickled by immersion for one hour in a 5% aqueous solution of sodium bicarbonate. The depickled calf-skin was then washed in running water for an hour and dried overnight in acetone. The calf-skin was then removed from the acetone, subjected to a blast of warm air to evaporate the acetone and then immersed for two hours in a treating bath at 130° F., the treating bath consisting of 50 parts by volume of succinyl chloride and 50 parts by volume of methyl "Carbitol" formal. The treated material was then removed from the bath, washed in acetone for two hours, removed from the acetone and allowed to dry. It was then immersed in a 5% solution of sodium bicarbonate in water until the skin reached a pH of about 7. The neutralized skin was removed from the neutralizing bath and washed in running water for two hours. At this time the calf-skin was found to be in a stable, nonputrescible condition in which it could be subjected to the usual operations following tanning.

Example 2.—A bated calf-skin was immersed overnight in acetone to dry it to a moisture content of about 10% determined as noted above. The dried calf-skin was then removed and the acetone was evaporated by a blast of warm air. After evaporation of the acetone the calf-skin was immersed in a treating bath at 130° F. for two hours, the bath consisting of 50 parts by volume of stearoyl chloride and 50 parts by volume of methyl "Cellosolve" formal. The treated skin was then removed and washed for two hours in a bath consisting only of acetone. The skin was then removed from the acetone, the acetone evaporated and the skin then immersed in a bath of 5% solution of sodium bicarbonate in water until the skin reached a pH of about 7. The neutralized skin was removed from the sodium bicarbonate solution and placed in a bath of running water for two hours, at which time it was removed and found to be in a condition resembling leather in which it could be subjected to the usual operations following tanning.

Example 3.—A bated steer-hide was immersed overnight in acetone to dry the hide to a moisture content of about 10% calculated as noted above. It was then removed and the acetone evaporated by a blast of warm air. The dried hide was then treated in a bath consisting of 50 parts by volume of di-glycollyl chloride and 50 parts by volume of methyl "Carbitol" formal. The treatment was carried out at 130° F. for a period of five hours. The treated hide was removed from the bath and washed for two hours in acetone and was then removed and the acetone allowed to evaporate. The hide was neutralized by soaking in a bath of 5% sodium bicarbonate in water until the skin reached a pH of about 7. The neutralized hide was removed and soluble materials removed by washing it in a bath of running water for two hours. The hide was found to be in a stable and nonputrescible condition suitable for conventional after-tanning treatment.

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

1. The method which comprises tanning dried hide having a moisture content of from 10% to

15% with an organic solvent solution containing from 10% to 50% by volume based on the volume of the solution of at least one member of the group consisting of acid chlorides of fatty acids having from 3 to 18 carbon atoms, di-acid chlorides of di-basic acids having from 4 to 10 carbon atoms, phenoxy acetyl chloride, m-sulfobenzoyl dichloride, trichloracetyl chloride, and chloracetyl chloride, the solvent being selected from the group consisting of the formal of the monomethyl ether of diethylene glycol and the formal of the monomethyl ether of ethylene glycol.

2. A method of tanning hide which comprises drying the hide by the solvent action of an organic liquid to bring the moisture content to from 10% to 15% and contacting the dried hide with an organic solvent solution containing from 10% to 50% by volume based on the volume of the solution of a member of the group consisting of acid chlorides of fatty acids having from 3 to 18 carbon atoms, di-acid chlorides of di-basic acids having from 4 to 10 carbon atoms, phenoxy acetyl chloride, m-sulfobenzoyl dichloride, trichloracetyl chloride, and chloracetyl chloride, the solvent being selected from the group consisting of the formal of the monomethyl ether of diethylene glycol and the formal of the monomethyl ether of ethylene glycol.

3. The method of tanning hide which comprises drying the hide by the solvent action of an organic liquid to bring the moisture content down to from about 10% to about 15%, contacting the dried hide with a solution of succinyl chloride in the formal of the monomethyl ether of diethylene glycol, the concentration of succinyl chloride in the solution being from about 10% to about 50% by volume based upon the volume of the solution, maintaining the hide in contact with the solution for a period corresponding to from about two hours for a calfskin to about four hours for a steer-hide at a temperature of 130° F., removing uncombined succinyl chloride by the action of a solvent, neutralizing acid compounds which may have formed within the hide, washing the hide to remove salts, and drying the hide.

4. The method of tanning hide which comprises drying the hide by the solvent action of an organic liquid to bring the moisture content down to from about 10% to about 15%, contacting the dried hide with a solution of stearoyl chloride in the formal of the monomethyl ether of diethylene glycol, the concentration of stearoyl chloride in the solution being from about 10% to about 50% by volume based upon the volume of the solution, maintaining the hide in contact with the solution for a period corresponding to from about two hours for calf-skin to about four hours for a steer-hide at a temperature of 130° F., removing uncombined stearoyl chloride by the action of a solvent, neutralizing acid compounds which may have formed within the hide, washing the hide to remove salts, and drying the hide.

5. The method of tanning hide which comprises drying the hide by the solvent action of an organic liquid to bring the moisture content down to from about 10% to about 15%, contacting the dried hide with a solution of diglycollyl chloride in the formal of the monomethyl ether of diethylene glycol, the concentration of digylcollyl chloride in the solution being from about 10% to about 50% by volume based upon the weight of the solution, maintaining the hide in contact with the solution for a period corresponding to from about two hours for calf-skin to about four hours for a steer-hide at a temperature of 130° F., removing uncombined diglycollyl chloride by the action of a solvent, neutralizing acid compounds which may have formed within the hide, washing the hide to remove salts, and drying the hide.

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