Patented Sept. 26, 1950 2,523,326

UNITED STATES PATENT OFFICE

2,523,326

TANNING WITH ORGANIC ISOCYANATES IN A NONAQUEOUS MEDIUM

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No Drawing. Application August 14, 1947, Serial No. 768,713

6 Claims. (Cl. 8—94.33)

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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 leather-like 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 isocyanates. These isocyanates 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 calfskins or steer hides, are very satisfactory. For most satisfactory treatment, the hide or skin should have

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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 terms "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 2 hours for calfskin to 4 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 16 hours in air at 105° C. It has been found that drying is most satsifactorily accomplished by the action of solvents, for example, acetone, methyl acetate (acetate of the monomethyl ether of ethylene glycol), 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 or hide is immersed in a body of the liquid treating agent and is maintained in the liquid for a sufficient period to convert the skin or hide to the new leather-like condition.

I have found that the isocyanates of aliphatic hydrocarbons having from 6 to 18 carbon atoms are effective to convert the skin or hide material to a leather-like condition. Among the compounds in this class are hexyl isocyanate, undecyl isocyanate and octadecyl isocyanate.

Other isocyanates which I have found effective to convert skin and hide material to leather-like condition are chloromethyl isocyanate, hexamethylene di-isocyanate, and 2,4-tolylene di-isocyanate.

These treating agents are ordinarily employed as solutions in organic solvents in order that they may penetrate well into the interior of the skin or hide material, and in order to avoid a too vigorous reaction between the material and the treating agent. Methyl "Carbitol" formal (formal of the monoethyl 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 (formal of the monomethyl ether of ethylene glycol) has been used as a 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 65% 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 vary 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 130° F. in a 50% solution of hexamethylene di-isocyanate in methyl "Carbitol" formal. In the case of steer hide, a four hour immersion in the same solution at 130° F. has been found satisfactory.

Comparable effects on these materials have been obtained within the same treating time using as treating agent a 50% solution of octadecyl isocyanate in tri-chlorethylene at room 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 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 trichlorethylene, 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 calfskin was depickled by immersion in a 5% solution of sodium bicarbonate for an hour and was then washed in running water for an hour. The skin was then immersed overnight in acetone to dry the skin to a moisture content of about 10% as determined above. The dried skin was then removed and the acetone evaporated by a blast of warm air. The skin was immersed in a treating bath at room temperature for a period of two hours, the treating bath consisting of a solution of 50 parts by volume of octadecyl isocyanate and 50 parts by weight of tri-chlorethylene. The treated skin was removed from the treating bath and washed for two hours in a bath consisting only of tri-chlorethylene after which it is removed and the tri-chlorethylene allowed to evaporate. The skin was neutralized to a pH of about 7 by immersion in a bath of 5% sodium bicarbonate solution in water. The neutralized skin was then removed from the sodium bicarbonate and washed in running water for two hours, at which time it was removed and found to be in a leather-like condition suitable for treatment by the usual operations following tanning of calfskin. The material so produced was found to have exceptionally high resistance to water.

Example 2.—Pickled calfskin was depickled and dried as in the preceding example and was subjected to a treating bath consisting of 20 parts by volume of 2,4 tolylene di-isocyanate and 80 parts by volume of methyl "Cellosolve" formal at 130° F. for two hours. The treated skin was washed in acetone for two hours, and was neutralized and washed as in the preceding example. There was obtained a stable and non-putrescible material suitable for treatment by the usual operations employed after tanning.

Example 3.—Pickled calfskin was depickled, washed, and dried as in Example 1 and was treated by immersion in a treating bath consisting of 50 parts by volume of hexamethylene di-isocyanate and methyl "Carbitol" formal at 130° F. for two hours. The treated skin was removed from the treating bath, washed in acetone, neutralized and washed as in Example 2. There was obtained a leather-like material in condition for further treatment by the usual operations following tanning.

Example 4.—A pickled calfskin was depickled, washed, and dried by the procedure of Example 1 and was then immersed for two hours in a treating bath consisting of 10 parts by volume of octadecyl isocyanate and 90 parts by volume of methyl "Cellosolve" formal at a temperature of 130° F. The treated skin was removed from the bath, washed in acetone, neutralized and washed in water as in Example 2. There was obtained a stable, non-putrescible, leather-like material in condition for treatment by the usual operations following tanning. The material is resistant to absorption of water.

Example 5.—A bated steer hide was dried by overnight immersion in acetone to dry the skin to a moisture content of about 10% as determined above. The dried skin was then removed and the acetone evaporated by a blast of warm air. The skin was immersed in a treating bath at room temperature for five hours, the treating bath being a solution of 20 parts by volume of octadecyl isocyanate and 80 parts by volume of tri-chlorethylene. The treated skin was removed from the treating bath and washed for two hours in a bath consisting only of tri-chlorethylene, after which it was removed and the tri-chlorethylene allowed to evaporate. The skin was then neutralized and washed in running water as in Example 1. There was obtained a stable, leather-like, non-putrescible material

suitable for treatment by the usual operations following tanning of a steer hide.

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

1. The method of tanning dried hides having a moisture content of from 10% to 15% which comprises contacting the skins or hides with an organic solvent solution from 10% to 65% by volume based on the volume of the solution of at least one member of the group consisting of isocyanates of aliphatic hydrocarbons having from 6 to 18 carbon atoms, chloromethyl isocyanate, hexamethylene di-isocyanate and 2,4-tolylene di-isocyanate.

2. The method of tanning hides which comprises drying the hides by the solvent action of an organic liquid to bring the moisture content down to from about 10% to about 15% and contacting the dried hides with an organic solvent solution of at least one member of the group consisting of isocyanates of aliphatic hydrocarbons having from 6 to 18 carbon atoms, chloromethyl isocyanate, hexamethylene di-isocyanate and 2,4-tolylene di-isocyanate, the concentration of the solution being from about 10% to about 65% of treating agent based upon the volume of the solution.

3. The method of tanning hides which comprises drying the hides by the solvent action of an organic liquid to bring the moisture content down to from about 10% to about 15%, contacting the dried material with an organic solvent solution of at least one member of the group consisting of isocyanates of aliphatic hydrocarbons having from 6 to 18 carbon atoms, chloromethyl isocyanate, hexamethylene di-isocyanate and 2,4-tolylene di-isocyanate, the concentration of the solution being from about 10% to about 65% of treating agent based upon the weight of the solution, removing uncombined compound by the action of a solvent, neutralizing acid compounds which may have formed within the hides, washing the hides to remove neutral salts and drying the hides.

4. The method of tanning hides which comprises drying the hides by the solvent action of an organic liquid to bring the moisture content down to from 10% to about 15%, contacting the dried hides with a solution of octadecyl isocyanate in tri-chloroethylene, the concentration of octadecyl isocyanate in the solution being from about 10% to about 65% by volume based upon the volume of the solution, maintaining the hides 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 octadecyl isocyanate by the action of a solvent, neutralizing acid compounds which may have formed within the hides, washing the hides to remove neutral salts, and drying the hides.

5. The method of tanning hides which comprises drying the hides by the solvent action of an organic liquid to bring the moisture content down to from about 10% to about 15%, contacting the dried hides with a solution of 2,4 tolylene di-isocyanate in the formal of the monomethyl ether of diethylene glycol, the concentration of 2,4-tolylene di-isocyanate in the solution being from about 10% to about 65% by volume based upon the weight of the solution, maintaining the hides in contact with the solution for a period corresponding to from about two hours for calfskin to about four hours for a steer hide at a temperature of 130° F., removing uncombined 2,4-tolylene di-isocyanate by the action of a solvent, neutralizing acid compounds which may have formed within the hides, washing the hides to remove neutral salts, and drying the hides.

6. The method of tanning hides which comprises drying the hides by the solvent action of an organic liquid to bring the moisture content down to from about 10% to about 15%, contacting the dried hides with a solution of hexamethylene di-isocyanate in the formal of the monomethyl ether of diethylene glycol, the concentration of hexamethylene di-isocyanate in the solution being from about 10% to about 65% by volume based upon the weight of the solution, maintaining the hides in contact with the solution for a period corresponding to from about two hours for calfskin to about four hours for a steer hide at a temperature of 130° F., removing uncombined hexamethylene di-isocyanate by the action of a solvent, neutralizing acid compounds which may have formed within the hides, washing the hides to remove neutral salts, and drying the hides.

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Certificate of Correction

Patent No. 2,523,326 September 26, 1950

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 3, line 44, after the word "treating" insert *agents and the rate of treating*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 24th day of April, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.