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3,048,929

METHOD OF DEHYDRATING HIDES

Filed Dec. 15, 1959

2 Sheets-Sheet 1

FIG. 1

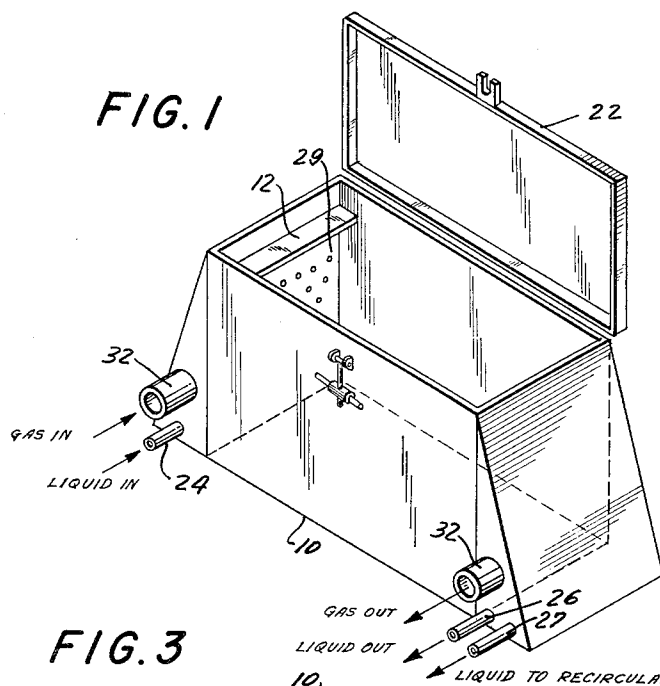
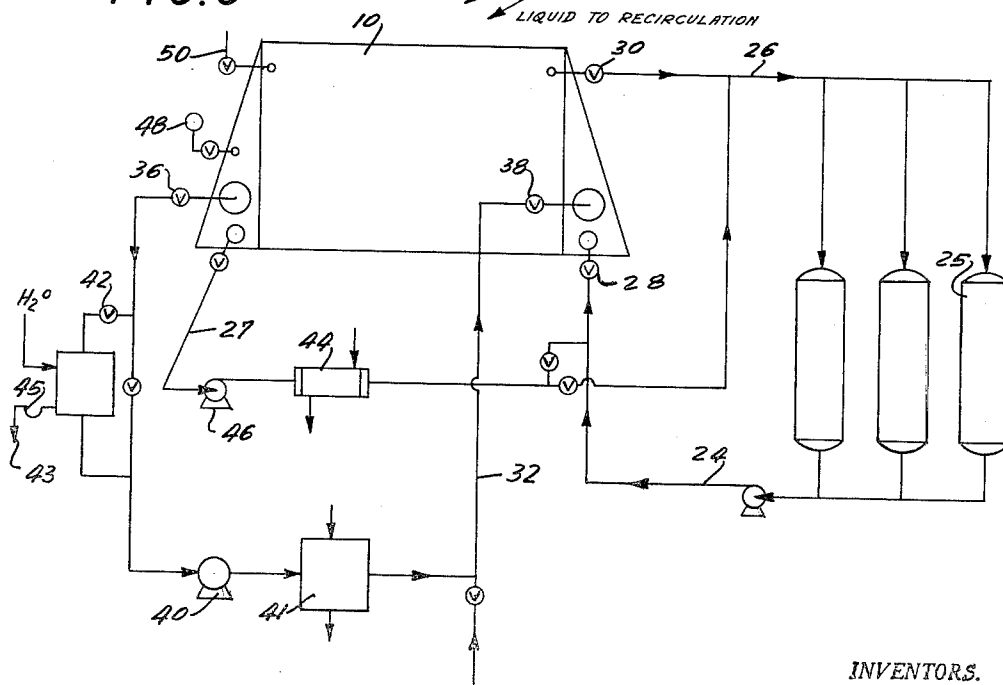


FIG. 3



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2 Sheets-Sheet 2

FIG. 4

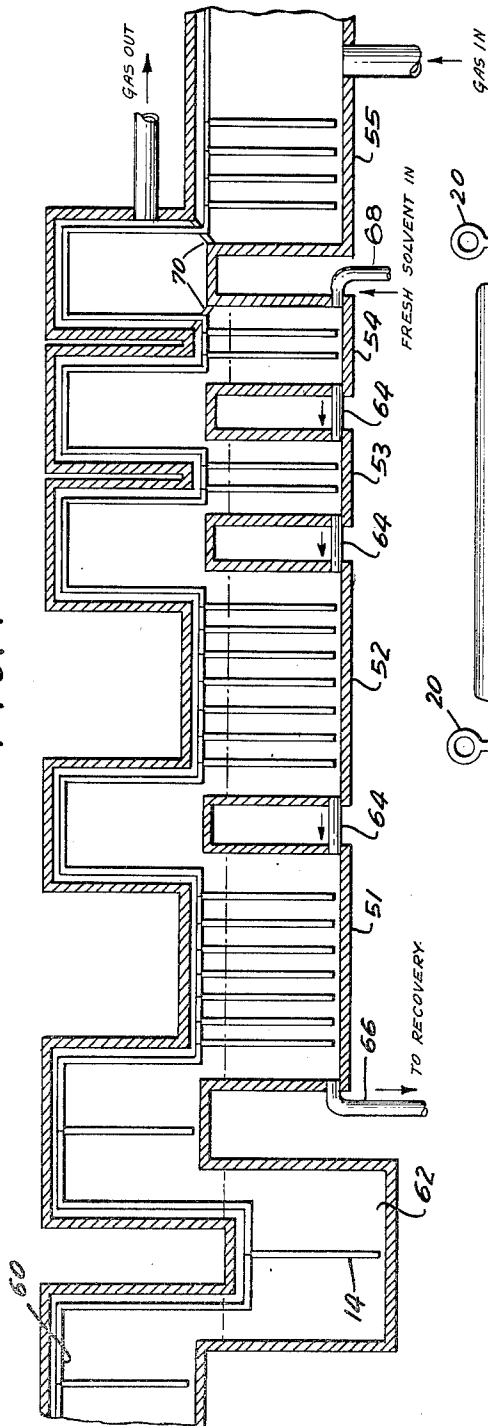
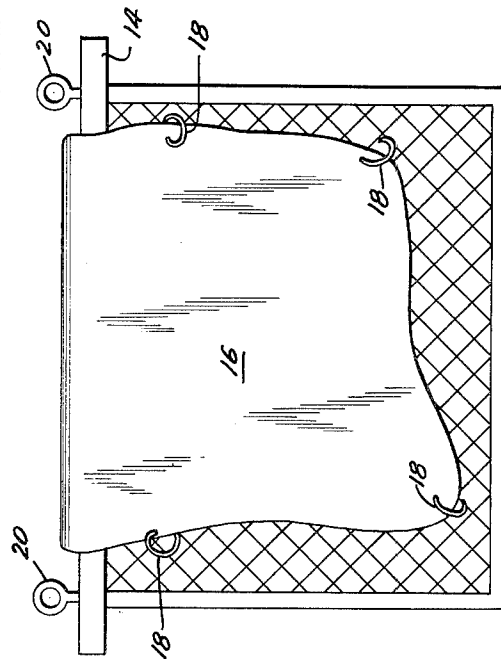


FIG. 2



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3,048,929

METHOD OF DEHYDRATING HIDES

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7 Claims. (Cl. 34-9)

This invention relates to a step in the process of converting animal hides and skins into leather. It is particularly directed to processes in which water-wet hides and skins are dehydrated by extraction of water with water miscible organic solvents of low boiling point, and the solvent is then evaporated from the hides.

Conventionally, vegetable tanned leather is prepared from animal hides by a long drawn out process. The raw hides from freshly butchered animals are salted to prevent spoilage, and shipped to the tannery. There, the cured hides are soaked to remove blood, salt, etc., and treated with lime to loosen the hair, which is then removed. At some point in the process, the hide is defleshed. The dehaired and defleshed hides are then "bated," which process also removes lime to some extent and leaves a hide wet with water; and the wet hides, consisting principally of hide fiber and water, are then exposed to the desired tanning liquid for the necessary time. The preparation of the hides takes about a week; vegetable tanning of thick leather takes about four four weeks or longer.

Many investigators in the field have suggested that the process could be speeded up by dehydrating the bated or otherwise prepared hides, and then applying the tanning agent in some organic fluid which could penetrate the hides more quickly. After the tanning agent penetrates the hide material, it is activated by immersion in water. Since drying of the hide material by evaporation of water produces an irreversible change in the hide substance, so that it can no longer be processed into acceptable leather, a number of investigators have suggested that the water could be extracted with a low boiling water miscible solvent, such as acetone, methyl alcohol or ethanol, and that after removal of the solvent, a dry plump hide material would be obtained ready for so-called "solvent tannage."

While excellent leather has been prepared in the laboratory using such drying procedures and following up with commercial tannage, the process has never become commercial, largely on economic grounds. When full hides are dehydrated by solvent extraction, it is extremely difficult, and most expensive in terms of solvent used, to completely dehydrate the hides. Even if the final solvent used leaves practically no free water in the hide (i.e., under 0.5% water), and the solvent is then evaporated under ordinary conditions, spots and horny areas will appear on the hide surface, due to localized action of water condensed from the ambient atmosphere on the hide surfaces. The action is intensified in ordinary practice, since it is extremely difficult to get all the free water out of the hide. These spots very often do not appear in laboratory tests on small hide segments, being more frequently observable as the size of the test pieces approach beef hide quarters.

Since the technique of complete dehydration is too expensive, methods have been proposed which aim to overcome the problem of horny spots on the hides. One such method involves removal of the solvent and water under reduced pressure, so that the temperature is kept very low. This method has never been successful commercially because of the high losses of solvent which inevitably occur in the process, the length of time required for dehydration, and the general high cost of vacuum distillation.

A second method for removing solvent water mixtures

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from hides without producing spotting has been suggested by us in our copending application Serial No. 535,755, now Patent No. 2,917,833, of which this application is a continuation-in-part. According to that invention, we found successful dehydration could be obtained by adding to the dehydration solvent an additive with polar groups in such proportions to carbon atoms that the hydrogen bonding ability of the resultant molecule was within a defined range. Butyl carbitol (mono-butyl ether of diethylene glycol) is the preferred additive, although a number of other alcohol ethers, and a number of alcohols, ethers and other compounds may be used.

While this method works well in operations of commercial size, it has certain economic disadvantages. The additives are expensive as compared with the dehydration solvents available. Furthermore, because of their high boiling points, they are somewhat difficult to recover in the solvent recovery operation. Hence, it would be commercially more desirable to operate a hide dehydration process without these additives.

The principal object of this invention is to provide a process for dehydrating hides by extraction of the water with a low-boiling water miscible organic solvent without an additive under such conditions that the process produces a smooth, plump, spongy dehydrated hides, without wrinkling or puckering of the hide surfaces, more rapidly and economically than by previous known methods.

We have made the surprising discovery that animal skins such as cattle hides can be dehydrated with a water miscible organic solvent selected from the group consisting of acetone and methanol, without the use of additives, rapidly and economically, with easy and substantially complete solvent recovery, and in a safe manner, to produce smooth, plump skins which absorb aqueous or non-aqueous treating solutions, provided the removal of water from the skins by the solvent, and the evaporation of the solvent from the skins thereafter, is carried out under certain carefully controlled conditions.

According to the present invention, we dehydrate water-wet animal hides and skins (which may be either freshly flayed washed hides at the packing house or bated dehaired hides ready for tanning) by extracting the water from the hides with a water miscible solvent of the group consisting of acetone and methanol, until the solvent-water ratio in the hide is at least 90 to 10, the final stage of the extraction being preferably carried out with solvent maintained between 110° F. and its boiling point. The hides and liquid extractant are then separated, and the solvent and water in the hides are evaporated by exposing them to a circulating stream of gas heated to 110 to 210° F. in a closed system, preferably with sufficient inert gas in the stream to render the mixture about the hides non-explosive, the gases being recirculated about the hides until they contain at least 25 mol percent of solvent vapor, and then circulated in part through a condenser to condense out part of the solvent while maintaining said minimum amount of solvent vapor in the gases about the hides until about 75% or more of the solvent has been evaporated. Thereafter, the solvent may be stripped from the hides as desired.

The process may start with hides from freshly slaughtered animals, which have been soaked in water to remove the blood and dirt, and preferably trimmed of most of the adhering flesh, the hides being dehydrated with the hair on. In such a process, the hide is also largely defatted while it is being dehydrated, and the finished hide is about one-third of the wet weight. Such a process eliminates the conventional salting of the fresh hides, which is necessary to preserve wet hides in shipment; and the resultant hides can be shipped at a considerable savings in freight costs. Better storage stability is

also obtained; the dehydrated hides can be stored for normal storage periods without deterioration.

The process can also be practiced on hides which have been dehaired and defatted, in conventional fashion, in the conventional tannery beam-house operations, and which have then been treated to remove the lime. Such hides, known as bated hides, are substantially free of hair and flesh, and comprise about 20% to 25% of hide substance, with the balance largely water.

The process may likewise utilize skins other than cattle hides, such as sheep skins and goat skins, although the principal problem in dehydration is with thick skins like cattle hides.

The solvent used for the dehydration may be acetone, methanol, or mixtures thereof. Small amounts of other low boiling water miscible organic solvents, boiling below the boiling point of water, may be used in admixture with the solvent, without interfering with the solvent recovery system or the efficiency of the dehydration. However, it is much simpler to use a single solvent system.

The process may be practiced in a batch or continuous fashion. In batch operation, the wet hides, mounted on frames, are set in a single tank, and the various treatments are conducted by changing the treating materials in the tank. In continuous operation, the hides are moved from operation to operation. The sequence of steps, however, is the same for both methods of operation, and, for the sake of simplicity, will be principally described as applied to a batch operation in a single tank.

The process may be understood by reference to the following drawings and description, which are provided by way of example and not by way of limitation. In the drawings:

FIG. 1 is a schematic view of a tank useful in practicing the invention.

FIG. 2 is an elevation of the hide mounting frame.

FIG. 3 is a flow sheet of a batch operation.

FIG. 4 is a flow sheet of a continuous operation.

Referring to FIGS. 1 to 3, we provide, on a closed rectangular tank 10 inner projections 12 on which may be hung mesh frames 14 on which hides 16 may be mounted, preferably maintained in tension by elastic clamps 18 hooked onto the hide and the mesh of the frame. The frames may be lowered into the tank, on removal of the lid 22, using hooks 20 provided for that purpose.

Solvent lines 24—26 are provided to permit solvent to be pumped from the solvent storage tanks 25 into and out of the tank; the lines are valved 28—30 close to the tank. The liquid enters the tank in back of a perforated plate 29 so that when it comes into contact with the hides, it is not surging.

A valved gas line 32 is provided for the addition of inert gas as required, with valved connections 36—38 to both ends of the tank; a blower 40 is provided to circulate gas through the line 32, and a heat exchanger 41 is provided in the line to heat or cool the gases as desired. A bleed-off valve 42, adjacent the gas line 32, is provided to remove volatiles from the system, taking them to a condenser 43, from which condensate may be removed through a trap or other condensate accumulator device 45 for transfer to a purification still (not shown).

The tank is provided with a liquid recirculation line 27 which contains coils 44 which may cool or heat the liquid therein, and a pump 46 for circulating the liquid as desired. A pressure gage 48 and a pressure relief valve 50 are also provided.

In the operation of the process, the tank is loaded with as many wet hides as it will hold, the system is closed and blanketed with inert gas and solvent added to cover the hides. Generally, the first stage of the water extraction is done with solvent-water mixtures left over from a previous second stage extraction liquid. The hides are permitted to come to equilibrium with the extracting liquid, the solvent-water mixture is removed and fresh liquid added, which contains a substantially higher solvent

to water balance than in the hide at this point. Generally, two or three extractions are needed to bring the solvent-water balance in the hide to 90% or more solvent. Each extraction takes 5 to 8 hours to reach equilibrium. The final stage of the extraction process is generally run for at least six hours to overnight, to insure final equilibrium.

At this point, some prior art workers have generally continued the extraction to attempt to remove all the water from the hides, a procedure requiring both time and expensive solvent. And prior art workers have evaporated solvent thereafter in various manners. Successful evaporation having hitherto been accomplished only by vacuum distillation at low temperatures, a high cost operation with inevitably poor solvent recovery.

According to the instant invention, at least the final stage of the liquid extraction of water from the hides is carried out at a temperature of at least 110° F. to somewhat below the boiling point of the solvent. Preferably, the temperature is about 120° F. to 130° F. This heating of the solvent produces two important results. First, it speeds up the final equilibrium between the body of the extracting solvent and that in the hide, so that actual equilibrium may be obtained in an hour or so. Secondly, it gets the hide temperature up, so that when the solvent is being evaporated from the hide, the effects of evaporative cooling are minimized.

Care must be taken not to use solvent at a temperature above 100° F. in the initial stages of the dehydration, as may result in damage to the skin. In general, moderate heating is safe when the solvent-water ratio in the skin is above 80—20, a temperature of at least 110° F. should preferably be maintained for at least the final hour of the dehydration, and may be maintained for as long as four hours in a twelve hour dehydration cycle.

The final solvent-water ratio must be at least 90—10, and is preferably in the range of 95—5 to 97—3. This latter range can generally be obtained with a total of three to four changes of extracting liquid in the batch process, and is easily obtainable in continuous counter-current operation.

In batch procedures, the solutions used in the various stages are pumped in and out of the tank to holding tanks. In a four stage operation, the first extracting solution will be half solution 1 from the preceding batch, half solution 2 from the preceding batch; the other half is pumped to the recovery still. Each of the remaining solutions will be half of the same solution from the last batch, half of the next higher solution; the final solution will contain half fresh solvent.

The times, temperatures and concentrations will vary somewhat depending on the weight, thickness and type of pretreatment of hides, the particular equipment used and the like. The object of these variations is to get a close approach to equilibrium between the exterior dehydrating solution and the fluid in the hides throughout the entire fiber structure thereof.

After equilibrium is reached in the final bath, the warm solvent is drained from the tank, steam is put through the coils 44, the valves 36 and 38 are opened, and the blower 40 is turned on to circulate the vapor coming off from the hides. Desirably, heated inert gas is added through line 32 to insure non-combustibility of the circulating gas.

As the gas, heated to between 110° F. and 210° F., circulates, its concentration of solvent vapor and water vapor builds up, and in a few minutes reaches a level of 25 mol percent; at this point the bleed-off valve 42 is opened, and a portion of the circulating stream is removed to the condenser 43. In general, once bleed-off is started, about 10 to 25% of the circulating stream can be removed, this being replaced by inert gas to prevent air leakage with the system. The rates are maintained to keep the solvent vapor concentration at a minimum of 25 mol percent to insure satisfactory recovery.

During the circulation, the temperature of the circulat-

ing stream in the system rises. At the beginning, the inert temperature of the gas stream may be 110–120° F., the outlet temperature about 95–100° F. As the desolventization progresses, these temperatures are increased to the upper end of the permitted range.

The recirculation generally produces a slight positive pressure in the system, which is preferably maintained. Good operating conditions generally produce about 1 to 5 p.s.i.g. pressure. The relief valves are set to prevent build-up of more pressure than the system will stand, and the operation should be carried out so that no solvent is lost due to opening of the relief valve.

The recirculation of the gas about the hides being desolventized has a number of effects which together insure the production of soft plump skins and economy of operation. The heating of the hides has insured uniformity in the composition of residual solvent, so that all areas of the hide surface react uniformly to the dehydration. The combination of warm hide and concentrated solvent vapor about the hide insures against shock localized evaporation, which induces cold spots due to evaporative cooling, with resultant water precipitation and localized damage to the hide surface. Finally, the build up of solvent vapor concentration makes possible relatively easy condensation, without refrigeration of the condenser water.

If desired, the process may be carried out in a progression of steps to provide what is essentially continuous operation. FIG. 4 illustrates a system in which such a process may be carried out.

A series of dehydration tanks 51, 52, 53, 54 is provided, together with a desolventizing tank 55. The racks 14 are carried on a conveyor 60, and enter the system through a water lock 62. Fresh solvent may be added as needed through liquid line 63 to tank 54; solvent may be moved as desired from tank to tank through liquid lines 64; and solvent may be taken through exit line 66 to a still for separation from added water. In ordinary practice, solvent is added continuously, to provide a continual movement of solvent through the tanks.

The desolventizing tank 55 is provided with sealing doors 70 to seal the tank off from the rest of the system. It is connected to gas lines just like the tank 10 in FIG. 3, to provide for the same type of operation.

In operating this continuous unit, the racks 14 are mounted on the conveyor, and go into the first tank 51 through a water trap 62. They are kept in each of the tanks 51–52–53–54 for long enough to get the desired equilibrium. The solvent in the last tank 54 is warmed to the desired finish temperature (preferably 110° F. up to the solvent boiling point, and more preferably 120–130° F.); the solvent in this tank is bled off to tank 53 while adding fresh solvent to maintain it at the desired finish level of 90%+ solvent, and preferably at 95 to 97% solvent, and 5 to 3% water. The racks are then lifted, the liquid draining back into the tank, and pass through the lock doors 70 into the desolventizer 55, where the solvent is recovered as in the batch process.

By varying the sizes of the tanks 51, 52, 53, 54, it is possible to vary the holding time and still keep the equipment operating at capacity. In general, the first two dehydrating baths will take longer to come to equilibrium than the last two, where the water content is low enough so that warm and hot solvent can be used, so that it is desirable to make tanks 51–52 substantially larger than tanks 53–54.

The following typical examples of the invention are provided by way of illustration and not by way of limitation.

Example I—Acetone Batch Dehydration

The apparatus of FIGS. 1 to 3 was used. Three water wet dehaired cattle hides (total wet weight about 200 pounds) were mounted on racks, placed in the tank, and water at 85° F. was added to fill the tank. The tank was sealed and the water drained to the sewer, the water being replaced by nitrogen. Thus, the system was effectively

purged of air. The common vent line between the treating tank and the solution storage tanks was then opened, and solution 1 (half solution 1-half solution 2 of a previous batch) was then pumped into the tank. The nitrogen from the treating tank was vented back to the solution storage tank, to keep the system jacketed with inert gas; the inert gas was moved back and forth throughout the procedure. 210 gallons of solution were used to cover the hides.

A series of four baths were used; the following table gives time of immersion, the temperature of the bath, and the initial and final specific gravities of the bath.

Bath	Time of Treatment	Temperature, ° F.	S.G. at 76° F./H ₂ O at 60° F. (Pure Acetone .787)	
			Initial	Final
1.....	5 hrs.....	85	0.828	0.847
2.....	5 hrs.....	85	0.796	0.805
3.....	6 hrs.....	85	0.791	0.794
4.....	Overnight.....	85	0.789	0.790

It will be noted that the final bath was held overnight for equilibrium; actually, equilibrium could have been attained in 6 to 8 hours.

The fourth solution was pumped back into the solution storage tank, and inert gas, heated initially to 110° F., was started circulating through the system, at the rate of 1000 c.f.m. (300 to 350 c.f.m. per hide). As the system warmed up, the inlet temperature was raised over a period of ten minutes to 160° F. It took about six minutes to reach the desired acetone concentration in the gas stream; at this point about 10% of the stream was by-passed into the condenser 43. Total desolventization time was about 70 minutes, with the top inlet temperature of the gas at 210° F. The specific gravity of the recovered solvent was just a bit higher than the gravity of the final solution, indicating that some bound water was removed.

The dehydrated hides were smooth, without any noticeable hardspots on their surface, indicating satisfactory solvent dehydration.

Example II.—Acetone Batch Dehydration Heated Final Baths

The procedure of Example I was repeated, but in this example bath 4 was heated to 120° F., resulting in heating of bath 3 to 95° F. It was noted that more rapid equilibrium was reached in the final bath, and that the desolventizing was speeded up somewhat.

The following table gives bath details.

Bath	Time, hrs.	Temperature, ° F.	S.G. as in Example I	
			Initial	Final
1.....	5	85	0.828	0.847
2.....	5	90	0.796	0.805
3.....	5	95	0.791	0.794
4.....	2	120	0.788	0.789

The desolventizing was carried out as before, but the initial entering gas could be heated to 150° F. without difficulty. This permitted the by-pass valve to be opened within a few minutes. On this run, a log was run of inlet temperatures, outlet temperatures, and the difference (ΔT) observed. The following results were obtained.

Time	Percent of Condensate Recovered	Inlet Temperature, ° F.	Outlet Temperature, ° F.	ΔT
10.....	16.4	170	129	41
20.....	46.4	196	144	52
30.....	67.5	207	154	53
40.....	81.9	203	154	49
50.....	90.6	208	164	44
55.....	98.4	203	169	34
60.....	100	193	166	27

It should be noted that in the latter half of the run, ΔT drops rapidly.

During the operation in both Examples I and II, the pressure built up to 4–5 p.s.i.g. The solvent lines in the system used were designed to permit operation at these low pressures, to insure against loss of solvent through the relief valve.

At the end of each run, the inert gas which still contains some acetone, may be passed through a scrubber or absorber, so that the tank may be safely opened.

The dehydrated hides of this example were at least as good as those of Example I.

Example III.—Methanol Dehydration

When methanol was used to replace acetone in the procedure of Example II, it was found that equilibrium times were slightly longer, and that desolventization likewise took longer, and somewhat more steam was required to get equivalent results.

The resultant dehydrated hides were completely satisfactory.

Example IV.—Continuous Dehydration (With Acetone)

A countercurrent dehydration was run in apparatus similar to that shown in FIG. 4, using washed hides from animals with hair on them, using only three baths, and moving the hides through the apparatus at the rate of 10 hides per hour. Warm acetone was added to the third bath at the rate of 2000 pounds per hour, and equivalent acetone water mixture was withdrawn from the first bath.

The holding time and temperatures of the baths were:

Bath	Holding Time, hrs.	Temperature, ° F.
1.....	8	90
2.....	8	100
3.....	2	120

In the desolventizing chamber, the cycle followed that described in Example II, except that the heating rate was somewhat slower. The hides were desolventized as batches, being withdrawn from the last bath every two hours; this permits the operators to move the batch of hides into the desolventizing tank, run the desolventizing cycle, and remove the finished hides from the racks if desired.

In a large scale operation, a system similar to that shown in FIG. 4 may be used. About 50 hides per hour can be handled without difficulty, feeding acetone to bath 4 at the rate of 10,000 pounds per hour. Baths 1 and 2 have a hold-up time of 7–10 hours, baths 3 and 4 of 1.5–2 hours each. Baths 1 and 2 are maintained at 90 to 95° F., bath 3 at 105° F. and bath 4 at 125° F. The hides are moved in batches of 50 each every 1.5 to 2 hours so that baths 1 and 2 have 250 hides in each, baths 3 and 4 and the desolventizing tank have 50 each.

While the examples are limited to beef hides, it is obvious that it is applicable to other animal skins and hides, either in the freshly slaughtered stage, or after curing, dehairing and bating.

As indicated above, hides and skins may be dehydrated by the processes of the instant invention at the packing plant, the process being used as a replacement for the conventional salting process. The resultant hides can be shipped most economically, weighing only about 30% of commercial salted hides; they keep indefinitely; and they can be treated by the tanner either in conventional fashion, after wetting back with water, or by impregnation with tanning materials in media other than water.

Alternately, the hides and skins can be dehydrated at the tannery after conventional preparation steps of fleshing, tanning, dehairing and bating. The dehydrated hides can, as in the first instance, be water tanned; but most

advantageously they are tanned by any of the solvent techniques known to the art.

This application is a continuation-in-part of our application Serial No. 535,755 filed September 21, 1955, now Patent No. 2,917,833.

What is claimed is:

1. The method of dehydrating water-wet hides and skins which comprises extracting water therefrom with a water-miscible organic liquid solvent selected from the class consisting of acetone and methanol, continuing the extraction and producing a solvent-water mixture about the hides until the solvent to water ratio within the hides is at least 90 to 10, removing the mixture thus produced from the hides, passing a heated stream of gas about the hides to vaporize solvent and water from the hides, recirculating the gas stream about the hides until the solvent vapor concentration in the gas is at least 25 mol percent, removing a portion of the solvent and water vapor from the recirculating gas stream while maintaining its solvent vapor concentration at at least 25 mol percent, until at least 75% of the solvent has been removed from the hides, and thereafter vaporizing the balance of the solvent from the hides.

2. The method of dehydrating water-wet hides and skins which comprises extracting water from the hides by contact with a series of water extraction baths consisting essentially of a water-miscible organic liquid solvent having a boiling point lower than water and selected from the class consisting of acetone and methanol, continuing the extraction and producing a solvent-water mixture about the hides until the solvent to water ratio in the hides is above 90 to 10, removing the mixture thus produced from about the hides, passing a stream of gas heated from 110° F. to 210° F. about the hides to vaporize solvent and water from the hides, recirculating the stream of gas in the system past the hides until the solvent vapor concentration in the gas is at least 25 mol percent, and thereafter withdrawing a portion of the circulating stream, and condensing solvent and water therefrom and returning the gas to the stream while maintaining a solvent vapor concentration of at least 25 mol percent in the main circulating stream until at least 75% of the solvent has been removed from the hides, and thereafter vaporizing the balance of the solvent from the hides.

3. The method of claim 2, in which the solvent to water ratio in the hides at the time of removal of the mixture is between 95 to 5 and 97 to 3.

4. The method of claim 2, in which the solvent is acetone.

5. The method of claim 2, in which the gas stream is recirculated about the hides under a slight positive pressure and the gas stream comprises an inert gas.

6. The method of claim 2, in which a series of at least three water-extraction baths is used, and in which the first two baths are maintained below 100° F., and the last bath is maintained at a temperature between 100° F. and the boiling point of the liquid in the bath.

7. The method of claim 5, in which the last bath is maintained between 120 and 130° F.

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