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DEHYDRATION OF UNTANNED SKINS WITH WATER-MISCIBLE ORGANIC SOLVENT CONTAINING A RELATIVELY NON-HYGROSCOPIC ORGANIC COMPOUND

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This invention relates to the preparation of leather from animal hides, and is concerned with tanning processes in which properly prepared hides are dehydrated prior to tanning. In particular, this invention relates to processes in which hides are dehydrated by treatment with water miscible organic solvents of low boiling point, and the solvent is then removed, and has as its principal object the preparation of smooth, spongy dehydrated hides in such processes. According to our invention, such dehydrated hides are obtained by including in the solvent used for dehydration a small amount of relatively non-hygrosopic organic addant having a boiling point of at least 150° C., and containing groups with marked hydrogen bonding characteristics.

Conventionally, vegetable tanned leather is prepared from animal hides by a long drawn out process. The cured hides are soaked to remove blood, salt, etc. and treated with lime to loosen the hair, which is then removed. The dehaired hides are then "bated," which process removes lime to some extent; 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 weeks or longer.

Many investigators in the field have suggested that the process could be speeded up by dehydrating the bated or otherwise prepared hide material, and then applying the tanning agent in some organic fluid which could penetrate the hide material 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 under ordinary conditions 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—e.g. acetone, methyl alcohol, methyl ethyl ketone etc.—and that after removal of the solvent, a dry plump hide material would be obtained ready for so called "solvent tanning."

While excellent leather has been prepared in the laboratory using such drying procedures and following up with solvent tanning, the process has never become commercial, largely on economic grounds. In order to remove all of the water from a hide, such large amounts of organic solvent are required that the process is too expensive. And if even a small amount of water is left in the hide prior to removal of the solvent, spots and horny areas, all indicative of the adverse effect of retained water, will appear in the hide on drying. These poorly dehydrated areas, which adversely effect subsequent processing and final leather quality, often do not appear in small laboratory tests, being more frequently observable only as the size of the pieces approach beef hide quarters. Consequently costs based on laboratory experiments are misleading, in that they suggest that suc-

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cessful dehydration can be obtained with less extracting solvent and in less time than is necessary in plant operations.

We have discovered that whole hides can be dehydrated successfully and economically by extraction with a water miscible low-boiling organic solvent, without the necessity for complete removal of water before drying, if there is added to the solvent a small percentage of an organic material having a relatively low vapor pressure at the boiling point of the dehydration solvent, and which contains a sufficient number of groups capable of hydrogen bonding relative to the number of carbon atoms so that the material lies within a range between insufficiently strong hydrogen bonding ability on the one hand, and too great hygroscopicity on the other. By empirical means, we have discovered that these limits can be defined by comparison with the properties of aliphatic compounds containing only primary alcohol and ether substituents, using the formula

$$N = \frac{400 + \frac{(a+1)^4}{2} + 120b^2}{n}$$

where

a is the number of ether groups,
b is the number of primary hydroxyl groups, and
n is the number of carbon atoms.

If *N* is below 50, the compound is too weakly hydrogen bonding to be useful in our method; if more than 90, the product is either too volatile or too hygroscopic. Optimum results are obtained in the range *N*=60 to 80. For primary aliphatic alcohols, the formula obviously becomes

$$N = \frac{400 + 120b^2}{n}$$

where

b is the number of primary hydroxyl groups and
n is the number of carbon atoms.

For aliphatic ethers, the formula obviously becomes

$$N = \frac{400 + \frac{(a+1)^4}{2}}{n}$$

where

a is the number of ether groups and
n is the number of carbon atoms.

The formula does not apply directly to compounds other than aliphatic ethers, alcohols and ether alcohols; but other compounds which have the same range between sufficient hydrogen bonding ability and too great hygroscopicity will work well in our process, as outlined below.

In considering the hydrogen bonding strength in relation to the formula, primary amine groups are roughly equivalent to primary hydroxyl, secondary amine groups are roughly equivalent to ether oxygens. Secondary hydroxyls are less effective than primary hydroxyls, but are much stronger than ether oxygens. Phenolic hydroxyls also possess good hydrogen bonding activity.

Even a fractional percentage of the addant shows some improvement in controlling the occurrence of spots and horny areas on hides. The amount needed for complete control depends on the amount of residual water left in the hide, and the precise hydrogen bonding characteristics of the addant. This becomes a matter of balancing economics. In general, about 1 to 4% of addant, based on the extracting solvent, will take care of about 2 to 15% of residual water in the hide, as measured in the solvent in equilibrium with the hide at the end of the extraction process.

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Acceptable results can also be obtained with lower concentrations of addant by controlling the rate of evaporation of the extraction solvent and water in the drying step, following extraction to the desired degree. This is preferably accomplished by recirculating a portion of the solvent-laden air coming off from the hide.

The use of very small quantities of formaldehyde, of the order of 0.1%, based on the weight of solvent, also helps to control the water spotting, and reduces the concentration of addant necessary to well under 1%.

While formaldehyde alone in various concentrations in the dehydrating solvent is useful in overcoming the adverse effects of retained water, it can quite often produce hides with a tender fiber and cracky grain. The combined use of formaldehyde in the above concentration range and small quantities of additive produce a uniquely beneficial effect, definitely superior to the action of formaldehyde itself or when such small concentrations of additive only are employed. Excellent dehydration with strong, supple fibers and grain character are obtained by the use of formaldehyde and the additive in combination, resulting in substantial economic savings in additive cost, and some desirable chemical and physical stability of the finished leather made from such dehydrated stock.

The addant itself may vary widely in chemical constitution, provided its hydrogen bonding strength and other molecular properties falls within the range indicated.

Example 1

As a typical example of our invention, three bated hides, weighing 88, 56 and 61 pounds respectively, are placed on racks and hung in an enclosed tank holding 225 gallons of solution (approximately 1600-1800 pounds). The weight of the dehydrated hides, which in the normal air dry state contain perhaps 15% moisture at equilibrium with the atmosphere, is in the range of 25-30% of the bated weight. Spent solution at 75° F. from a previous dehydration (containing approximately 79.5% acetone, 2% butyl carbitol—i.e. mono-butyl ether of diethylene glycol, balance water and other substances picked up from previous lots of hides), is run into the tank to cover the hides; agitation is obtained by circulating the liquid through the tank with a pump. After ten minutes, the solution is withdrawn; its acetone content will be down to 76%.

An intermediate liquor from a previous bath is now run in, at 75° F. and 86% acetone concentration. It is gradually warmed to 95° F.; extraction is continued for three hours and the liquor withdrawn at 80.6% acetone content. Fresher liquor from a previous batch at 94.5% acetone content and 95° F. is next run in, and dehydration continued for three more hours, to 93% acetone content. Finally, a batch consisting mainly of fresh acetone (98%) with 2% butyl carbitol is run in at 95° F. and dehydration continued for three more hours; the acetone content is down to 97%.

During this entire period of approximately ten hours (including pumping time) the tank is blanketed with nitrogen.

The treating tank is then connected to a drying system, comprising a blower, a scrubber in which acetone is absorbed in water, and a heater in series with the treating tank, with a by pass around the absorber. An airflow of 1100 c.f.m. is maintained, and the entire flow by passed around the scrubber and recirculated for about ten minutes, until the heater has raised the temperature sufficiently to evaporate a substantial amount of acetone.

As the temperature rises and the concentration of acetone vapor in the system rises, the system pressure rises appreciably. This rise in pressure may be used to advantage; it assures better circulation of air around the hides in the treating tank. Further, it is then possible by the use of a suitable absorber, scrubber, or condenser, to recover the evaporated acetone from the gas

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stream in good yield, with somewhat smaller equipment, by bleeding a small but steady stream of acetone laden vapor from the system through the recovery unit. The rate of bleeding is controlled so that the pressure in the system is maintained within desired limits consistent with good recovery efficiency and quality of dehydrated stock. Pressures will run in the range of 0-5 lbs. (gauge) and temperatures in the eventual range of 200° F. are used to accomplish a thorough desolventizing in an hour's time. In our system for reasons of safety, the atmosphere at the start of the desolventizing is practically all nitrogen, but since it is a closed system, there is little loss of this gas.

At this stage the hides are ready for tannage by treatment with solvent tanning solutions. They are white, plump, smooth, stronger and porous in texture and appearance, and they are approximately equal in thickness and area to the original bated stock.

Example 2

A similar run was made, except that the solutions used contained 83%, 88%, 95% and 97% acetone respectively at the start of each cycle, and the liquors heated to 100° F.; the total dehydration time was only nine hours. Desolventizing was done as in Example 1.

Example 3

Faster dehydration can be obtained by using 95% acetone (+ butyl carbitol) in the first treatment, and 98% acetone (+ additive) in the next two treatments. Total dehydration time can be reduced to about 5 to 6 hours; but this means considerably more still capacity to recover acetone from the water acetone mixture.

Example 4

6 bated sides, weighing a total of 201 pounds wet, were treated in the tank with 220 gallons of water containing 10 pounds of ammonium sulfate at 70° F., the initial pH of the solution being about 5.0. The pH rose rapidly to about 7.5, while the solution was agitated by pumping through the tank. After 6 hours, agitation was stopped, and the hides were kept in the water overnight. Circulation was resumed for three hours in the morning. The water was drained; the resultant delimed hides were well plumped, and had a slick grain.

The tank was then filled with a spent batch from a previous dehydration, containing about 83% acetone and about 0.4% butyl carbitol, and the extraction run for 20 minutes at 88° F. A second extraction solvent containing 88% acetone and 0.4% butyl carbitol was used for 3½ hours at 88° F.; the third extraction liquid, containing 95% acetone and 0.4 butyl carbitol, was run for three hours; and finally 220 gallons of fresh acetone containing 3 liters of butyl carbitol (about 0.4%) and 2 liters of formalin, (40% formaldehyde, equal to approximately 0.1% formaldehyde in the 220 gal.) was used to extract the hides for 3 hours at 70 to 90° F.

The acetone was drained, and desolventizing was accomplished as in Example 1, building up the pressure in the system to 5 p.s.i. over a 30 minute period before bleeding any gas to the solvent recovery system. Desolventizing was complete in 90 minutes. The stock was full, plump and smooth, and in excellent condition for further treatment.

A convenient technique for introducing additive into the dehydrating solution is to add it to the last bath only as shown above. Our analytical data indicates that there is little preferential uptake of additive, so its concentration does not change very much as the bath is re-used. The formaldehyde however is nearly exhausted each time it is used as it combines preferentially with the stock, so that the re-used baths contain little HCHO.

It is not essential that the first extracting baths contain addant; its presence is essential only in the last bath, which impregnates the hide with the liquid which is evap-

orated from the hide. But it is most convenient and economical to re-use dehydrating solutions which contain addant from the time they were initially prepared. Furthermore, the use of addant in the earlier liquors insures more uniform distribution of addant in the hides during desolventizing.

We have dehydrated hides without recirculation. Although faster initial drying is obtained, the rapid evaporation of the acetone cools the hides, so that little time is saved by not recirculating. And, as pointed out above, it is necessary to use more additive to obtain good dehydration.

Butyl carbitol is one of the preferred addants for the control of spotting in our process; it has an N value of 70 according to our empirical equation. But a host of other compounds can be used, provided the ratio of hydrogen bonding activity to the number of carbon atoms is within the limits indicated by the formula.

Comparisons between series of compounds are useful in understanding our result. Thus, various ethers of ethylene glycol (the "Cellosolves") were compared for effectiveness in our process, using in each case 0.1 mol of compound per kilogram of acetone to dehydrate .15 kgm. of wet stock.

Ether	B.P., ° C.	"N"	Results
Methyl Cellosolve.....	125	176	Poor.
Ethyl Cellosolve.....	135	132	Do.
Butyl Cellosolve.....	171	88	Fair.
Hexyl Cellosolve.....	208	66	Very good.

Similar trials were made with the mono-ethers of diethylene glycol (the "Carbitols"), with the following results.

Ether	B.P., ° C.	"N"	Results
Methyl Carbitol.....	194	112	Poor.
Ethyl Carbitol.....	195	93	Poor to fair.
Butyl Carbitol.....	231	70	Excellent.
Hexyl Carbitol.....	259	56	Good.

A group of n-alcohols were then compared, with the following results.

Alcohol	B.P., ° C.	"N"	Results
n-hexanol.....	157	87	Fair.
n-heptanol.....	176	74.5	Very good.
n-octanol.....	195	65	Good.
n-nonanol.....	213	58	Good-fair.
n-decanol.....	231	52	Fair.
n-dodecanol.....	255	43	Poor.

Note that results improve, as the number of carbon atoms and boiling point go up, to a maximum at n-heptanol, and then go down as the ratio of hydrogen bonding activity to carbon atoms goes down.

The boiling point is only important as it pertains to the volatility of the material at the desolventizing temperature, and the tabulated data clearly shows that high boiling point alone is not a guarantee of potency as a dehydration aid. However, all compounds with N=50 to 90 have boiling points above 150° C.

A group of eight carbon atom compounds having a single primary hydroxyl, and 0, 1, 2, and 3 ether oxygens, was compared, with the following results.

Compound	OH	Ether (O)	C	N	Results
n-octanol.....	1	0	8	65	Good.
hexyl Cellosolve.....	1	1	8	66	Very good.
butyl Carbitol.....	1	2	8	70	Excellent.
ethoxy triglycol.....	1	3	8	81	Good.

Note how the rating increases with added hydrogen bonding strength to a maximum at butyl Carbitol, and

then goes down as the hydrogen bonding/C atom ratio goes above the optimum point.

As indicated above, the presence of hydroxyl is not essential for good results; the following ethers are typical.

Ether	OH	Ether (O)	C	N	Results
dibutyl ether.....	0	1	8	51	Poor.
vinyl butyl Cellosolve.....	0	2	8	55	Fair to poor.
diethyl Carbitol.....	0	3	8	66	Very good.
dibutoxy tetraglycol.....	0	5	16	65.5	Do.
dioxane.....	0	2	4	110	Poor.

The addants used need not be of low molecular weight, nor need they even be liquid—they need only be soluble in the solvent employed, and have the correct hydrogen bonding characteristics. For example, the polyalkylene glycols of high molecular weight, which are widely used as surfactants, and which range from viscous liquids to solids, are effective in our process. We have used "Ucon HB5100"—a high molecular weight polyalkylene glycol sold by Carbide and Carbon Chemicals Co.; various "Carbowax" materials, sold by the same company, and which are methoxy poly ethylene glycols, and a large number of non-ionic detergents of similar chemical composition.

Good or better results are obtainable with classes of compounds other than alcohols, ethers and alcohol-ethers. Phenol, the cresols, and many of the alkylated and arylated phenols are useful. In the case of aromatic compounds, our empirical formula is of course not directly applicable—the phenolic hydroxyl groups differ in hydrogen bonding ability from primary aliphatic hydroxyl groups, while at the same time the aromatic carbons would have a different value in the formula.

The H-bonding characteristics of phenols is largely governed by the resonance in the aromatic ring; alkyl or aryl substitution beyond one or two carbon atoms does not cause any marked decrease in hydrogen bonding, so that all the alkyl and aryl substituted phenols we have tried (we have gone up to amyl phenol and p-phenyl phenol) are very similar to phenol and cresol in our process, being essentially like the hexanols—fair to good in our process.

Certain weak organic acids can also be used e.g. 2-ethyl hexanoic acid, p-methyl benzoic acid, p-methoxy benzoic acid; these give fair to good results. Aldehydes and ketones can likewise be used.

The amines follow the same rules as corresponding alcohols and ethers; thus, 2-ethyl hexyl amine is good, while triethylene tetramine is far too hygroscopic, and gives poor results.

Obviously, other compounds having hydrogen bonding activity falling within the indicated range can be used in our invention, which is set forth in the claims. While the examples all relate to the dehydration of full cowhides, which are intended for use in the preparation of vegetable tanned sole leather, the methods are obviously useful wherever it is desirable to obtain a water free hide of any description.

We claim:

1. In the method of dehydrating water-wet untanned hides which comprises extracting the water from the hides with a low-boiling, water-miscible, inert organic solvent, the improvement which comprises ending the extraction at a point where the hides contain from 2 to 15% residual water, at least the final extraction of water being done with a low-boiling, water-miscible, inert organic solvent containing 0.4 to 4% of a relatively non-hygroscopic addant having a boiling point of at least 150° C., and which is a compound soluble in the solvent and selected from the group consisting of:

(a) aliphatic alcohols, aliphatic simple ethers, and aliphatic ether alcohols containing only carbon, hydrogen, and oxygen, and in which the oxygen is present as a radi-

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cal of the group consisting of primary hydroxyl and ether, the ratio of said radicals to carbon being such as to yield $N=50$ to 90 in the formula

$$N = \frac{400 + \frac{(a+1)^4}{2} + 120b^2}{n}$$

where

a is the number of ether radicals

b is the number of primary hydroxyl radicals

n is the number of carbon atoms; and

(b) phenol, alkyl substituted phenol containing up to five carbon atoms in the alkyl substituent, phenyl substituted phenol, 2-ethyl hexanoic acid, p-methyl benzoic acid, p-methoxy benzoic acid, and 2-ethyl hexyl amine; separating the hides from the liquid, and evaporating the absorbed solvent and residual water from the hides with a stream of heated gas.

2. The method of claim 1, in which the absorbed solvent and residual water are evaporated from the hide by means of a circulating stream of heated inert gas.

3. The method of claim 1, in which N is between 60 and 80.

4. The method of claim 1, in which the low-boiling solvent is acetone.

5. In the method of dehydrating water-wet untanned hides which comprises extracting the water from the hides with a low-boiling, water-miscible, inert organic solvent, the improvement which comprises ending the extraction at a point where the hides contain from 2 to 15% residual water, at least the final extraction of water being done with a low-boiling, water-miscible, inert organic solvent containing 0.4 to 4% of a relatively non-hygrosopic aliphatic ether alcohol having a boiling point of at least 150°C ., soluble in the solvent and containing only carbon, hydrogen, primary hydroxyl oxygen and ether oxygen, the ratio of oxygen-containing radicals to carbon being such that $N=50$ to 90 in the formula

$$N = \frac{400 + \frac{(a+1)^4}{2} + 120b^2}{n}$$

where

a is the number of ether radicals

b is the number of primary hydroxyl radicals

n is the number of carbon atoms;

separating the hides from the liquid and evaporating the absorbed solvent and residual water from the hides with a stream of heated gas.

6. A method of claim 5, in which N is between 60 and 80.

7. The method of claim 5, in which the ether alcohol is diethylene glycol mono-butyl ether.

8. In the method of dehydrating water-wet untanned hides which comprises extracting the water from the hides

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with a low-boiling, water-miscible, inert organic solvent, the improvement which comprises ending the extraction at a point where the hides contain from 2 to 15% residual water, at least the final extraction of water being done with a low-boiling, water-miscible, inert organic solvent containing 0.4 to 4% of a relatively non-hygrosopic aliphatic alcohol having a boiling point of at least 150°C ., soluble in the solvent and containing only carbon, hydrogen, and primary hydroxyl oxygen, the ratio of the hydroxyl radicals to carbon being such that $N=50$ to 90 in the formula

$$N = \frac{400 + 120b^2}{n}$$

where

b is the number of primary hydroxyl radicals and n is the number of carbon atoms;

separating the hides from the liquid and evaporating the absorbed solvent and residual water from the hides with a stream of heated gas.

9. In the method of dehydrating water-wet untanned hides which comprises extracting the water from the hides with a low-boiling, water-miscible, inert organic solvent, the improvement which comprises ending the extraction at a point where the hides contain from 2 to 15% residual water, at least the final extraction of water being done with a low-boiling, water-miscible, inert organic solvent containing 0.4 to 4% of a relatively non-hygrosopic aliphatic ether having a boiling point of at least 150°C ., soluble in the solvent and containing only carbon, hydrogen, and ether oxygen, the ratio of ether radicals to carbon being such that $N=50$ to 90 in the formula

$$N = \frac{400 + \frac{(a+1)^4}{2}}{n}$$

where

a is the number of ether radicals, and n is the number of carbon atoms;

separating the hides from the liquid and evaporating the absorbed solvent and residual water from the hides with a stream of heated gas.

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