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ALDEHYDE TANNING OF LEATHER

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This invention relates to the formaldehyde tanning of leather, and aims to provide such a leather which has the advantages of formaldehyde tanned leathers, without the usual attendant disadvantages of a brittle and cracky grain which resists finishing operations.

Formaldehyde is a tanning material which is soluble in water and most organic solvents. It is commercially available both in aqueous solution (formalin), in solution in organic solvents, and as polymers which readily depolymerize to yield the active monomer. It is a very active tanning agent for hide substance, as regards its ability to impart chemical and hydrothermal stability to hide fiber. It is also capable of stabilizing other tannages, such as mineral and vegetable tannages. It has the additional advantage that it yields white tanned leather, and such white leathers yield exceptionally bright colored dyeings.

The one factor that has limited the use of formaldehyde has been the difficulty of obtaining proper distribution through the vertical cross-section of the hides being tanned. Where the leather is of any substantial thickness, the surface is generally over-tanned with respect to the interior. The result is usually a leather with a brittle and cracky grain, which resists all efforts to work it into the desired commercially smooth surface. As a result, formaldehyde tanning has been restricted commercially to thin leather, such as glove leathers, of thicknesses under about 3/48 inch (1/48 inch is called an "iron" in the leather trade).

According to our invention, we can obtain formaldehyde tanned thicker leathers which have the desirable properties obtained with formaldehyde tanning, without the brittle and cracky grain, by treating porous dry untanned hide substance with an impregnating solution of formaldehyde in an organic solvent containing insufficient water to give the typical astringent reaction between hide substance and aqueous formaldehyde, then rinsing the hide substance with a similar formaldehyde solvent containing substantially less formaldehyde than the impregnating solution, and then treating the hide substance with water to cause the formaldehyde to completely react with and tan the hide substance. Preferably, both the impregnating solvent and the rinsing solvent are water-miscible; the lower alkyl ketones and alcohols are preferred solvents.

The leather produced by the method of this invention is characterized by having more formaldehyde combined with hide substance in the interior of the leather than in the flesh and hide layers. Characteristically, when a standard shrink temperature test is run on leather made in accordance with the invention, the leather forms a barrel shaped piece instead of an hour-glass shaped piece, as is the case with conventional leathers.

This standard shrink temperature test is described in American Chemical Society Monograph No. 101, McLaughlin and Theis, The Chemistry of Leather Manufacture, Reinhold Publishing (New York) 1945, at page 783. A piece of leather 0.5" x 3" is clamped and set in a bath of acidulated water (for vegetable tanned leather) or aqueous glycerol (other leathers) and the bath temperature raised in standard fashion. As the test proceeds, the leather first swells as it absorbs the liquid and then, at the shrink temperature, starts to shrink. Since the lesser tanned leathers will shrink first, a conventional leather test piece which has more tan near the outside, will yield a finished test piece whose cross-section is hour-glass shaped, whereas leathers made in accordance with this invention yield pieces which are barrel shaped in cross-section.

It should be noted that formaldehyde, once it impregnates, is difficult to rinse from the interior of the hides, being washed out well for only about .02 inch from the surface (this approximates one iron=1/48 inch). Obviously, leather which is thinner than about 3 irons, will not show the notable difference between interior and surface characteristic of the present invention.

Where ordinary thick leathers, such as sole leathers, have specific gravities of 1.0 or more, it is possible to produce formaldehyde tanned sole leathers, in which some impregnant is used to give the leather other desirable properties, with a specific gravity as low as 0.65, and still have a leather which is resistant to compacting by the pressure applied by the rollers used in the finishing operation. In general, thinner formaldehyde tanned leathers made in accordance with this invention will have specific gravities of the order of 0.75 or less.

To obtain porous untanned hide substance, it is necessary to extract the water from untanned hides. The preferred method of extracting the water involves immersion in aqueous water-miscible low boiling liquids like methanol, ethanol, the propanols, acetone, etc., which extract the water from and replace it in the hide. When sufficient water has been replaced so that the water left will not damage the hide during evaporation, the hide is desolventized by evaporation. Such a process is described in the copending Kremen and Southwood application Serial No. 535,755 filed September 21, 1955, now U.S. Patent No. 2,917,833, where the extracting liquid is mixed with an addant such as butyl carbitol (diethylene glycol monobutyl ether).

Formaldehyde may be put into the hide substance during such a process of hide dehydration, provided it is not added until the water concentration in the hide is reduced below a point where a typical aqueous astringent tannage occurs. Thus, a hide comprising about 25% hide substance and 75% water may be extracted with a liquid like acetone, in admixture with some water, to produce a hide containing a liquid comprising about 75% acetone–25% water. In such a system, it is inadvisable to add formaldehyde to the first bath, since the formaldehyde will react with the hide substance. However, once the solvent-water ratio is up to 75%–25% in the hides, it is reasonably safe to add the formaldehyde.

Example I—Addition of formaldehyde during hide dehydration

Thus, a group of wet cow hides was dehydrated by exposing them to four successive acetone treatments, using a large excess of treating solvent. The wet hides were extracted with 81% acetone and water, obtained from a previous second stage of dehydration; the hides, after coming to equilibrium with the fluid, contained acetone and water in the ratio 76–24. They were then treated with 93% acetone, from a previous third stage, and came to equilibrium at 81% acetone–19% water. 97% acetone from a previous fourth stage was used on the third stage and a 93% acetone-7% water ratio was obtained at equilibrium. Fresh acetone, in the fourth stage, increased the acetone-water ratio in the hide to 97–3.

In the practice of our invention with such a process, we have added 0.5, 1.0, 2.5 and 5.0% of formaldehyde (in the form of 55% formaldehyde solution in methanol)

based on solution weight, to the 93% acetone-water mixture used in treating the hides in the second stage of dehydration. The 97% third stage bath, and the pure acetone used in the fourth stage, act to rinse out formaldehyde from the surface of the stock. The resultant hides, after evaporation of the solvent, can be treated with water to get material which is well tanned in the interior and just barely tanned to untanned at the surface, and which yield barrel shaped shrink pieces at very low temperatures.

Somewhat less formaldehyde is needed when the formaldehyde is added to the third bath, and the pure acetone of the fourth bath is used as a rinse, to get equivalent tannage. By using higher concentrations of formaldehyde (2.5% to 5%) in the third bath, and rinsing only with pure acetone, a fair degree of surface tannage is obtained. Similar results may be obtained with lower amounts of formaldehyde in the third bath, and very low amounts of formaldehyde (0.1% or less) in the final rinse. Care must be taken, however, to avoid too much formaldehyde in the surface, or grain crackiness will result.

It is preferable to combine the formaldehyde tannage with some other form of tannage, using the formaldehyde to stabilize the other tannage. This can be done in various ways. One way is to treat unfinished leather, already tanned by vegetable extracts or by syntans.

Example II—Formaldehyde tanning of tanned leather

An unfinished sole leather, 9 irons thick and still porous because of its lack of finish, was dipped into a solution containing 2% formaldehyde, added as a 55% solution in methanol, the balance being isopropanol. It was rinsed with clear isopropanol, and the isopropanol replaced with water. The resultant leather, on finishing, showed much greater resistance to compacting than leather not so treated; where the untreated leather required extensive treatment with fillers to resist compacting, the treated leather finished well with much less filler. It showed a barrel shaped cross-section when exposed to the shrink temperature test.

Another way to combine tannages is to impregnate untanned hide substance with both formaldehyde and other tanning agents; thus

Example III—Combined formaldehyde vegetable tan

A cow hide was dehydrated as in Example I, adding 2% formaldehyde to the third bath, and rinsing with pure acetone. It was then desolventized by evaporating the acetone; the formaldehyde not rinsed from the surface remained bound to the interior of the hide.

The dry porous dehydrated hide was treated with a solution comprising

	Parts by weight
Quebracho extract (20% water-80% solids)	5
Dymerex resin (dimerized rosin)	20
Paraffin wax (melting point 50° C.)	10
Acetone at 120° F	65

and allowed to remain 15 minutes to ensure complete impregnation.

The hide was drained and immersed in a solution comprising

1 part by weight of above.
4 parts by weight of acetone at 120° F.

After 10 minutes, the hide was withdrawn, then immersed in water for several hours and dried.

The resultant unfinished leather was about as thick as the original hide (9 to 10 irons), had good abrasion resistance and low water uptake (due to the resin), specific gravity of 0.65. It had a high shrink temperature and gave a barrel shaped test piece. It shows more resistance to compacting than conventional quebracho tanned sole leather.

It is somewhat better practice to dehydrate without formaldehyde, and add both tans together; thus

Example IV—Combined formaldehyde vegetable tan

Example III was repeated, except no formaldehyde was added during the dehydration. Instead the impregnation bath used to treat the dry porous dehydrated hide was modified by removing 5 parts of acetone, and substituting 5 parts of formcel, a solution of 55 parts of formaldehyde in 45 parts of methanol; the rinse solution used was the impregnation solution diluted with 4 parts its weight of acetone.

The leather was very similar in properties to the leather of Example III, except that it was somewhat more resistant to compacting and had a slightly harder grain surface.

The combination tanning is preferably combined with the use of impregnants to give the leather additional properties as described in copending application Serial No. 729,238 filed April 18, 1958.

Example V—Combined formaldehyde vegetable tan

Example IV was repeated, except that the rinse consisted of

	Parts by weight
Quebracho extract	5
Dymerex resin	4
Paraffin wax (50° C. melting point)	2
Formcel	1
Acetone	88

In this leather, the quebracho was kept at the same high level in the surface as in the interior. Its properties were very similar to the leather of Examples III and IV, except that the color of the surface more nearly resembled that of conventional tanned leather.

A particularly useful leather can be made by impregnating the interior of the leather with a resin, while tanning the interior of the leather with formaldehyde, rinsing these impregnants largely from the surface, and then tanning the surface layers with quebracho. Such a leather can be made as follows:

Example VI—Formaldehyde tanned leather with a surface quebracho tan

Example II was repeated, except that the impregnating solution consisted of

	Parts by weight
Dymerex resin	20
Paraffin wax (melting point 50° C.)	10
Methyl formcel (55% formaldehyde, 45% methanol)	5
Distilled fatty acids (oleic-stearic) mixture	2.5
Acetone	62.5

and the rinse solution consisted of 20% of this impregnating solution, 80% acetone. After the final immersion in water to activate the formaldehyde tan, the wet hide was immersed for one hour in lukewarm water containing 10% of a powdered bisulfite-quebracho extract, at pH 3 to 4. After this immersion, the hide was drained and dried. The resultant leather had a surface color and character about identical with conventional quebracho tanned sole leather. However, it was much more water resistant than either conventional leather or the leather of Example III, since the hydrophilic quebracho was present only in the surface layers of the leathers. As a result, only the surface was wettable, an ideal situation, since the surface must be wettable for rolling in the finishing operation, whereas a hydrophobic interior makes the leather highly resistant to penetration by water.

Leathers can be made with a wide variety of impregnants; substantially all natural and synthetic resin, cellulose derivatives, soluble waxes and natural and synthetic rubbers can be used, provided they can be put into solution. Preferably those which can be put into mutual

solution with formaldehyde are used for the practice of this invention.

Typical of other resins useful are the following:

Example VII

A series of resins was tested on pieces of hide dehydrated as above without the use of formaldehyde. In each case the formula used was as follows:

	Parts by weight
Resin	20
Formcel (55% formaldehyde, 45% methanol)	5
Acetone	75

In each case, the dehydrated hide was immersed in the solution of resin and then rinsed in a rinse comprising

	Parts by weight
Original solution	20
Acetone	80

After rinsing, the solvent was extracted with water containing 1% formaldehyde, and the piece dried. Resin uptake varied from 20% to 30%, except as indicated below; the formaldehyde tanned leathers resulting were all water-resistant and firm. Comments show differences from the sample made from Dymerex resin.

Resin	Uptake, percent	Comments
¼ second nitrocellulose	16	Very pale color.
Manila gum MA	24	
Clorafin 42-S (Chlorinated paraffin 42%)	22	Leather softer than Dymerex.
Vinylite VAGH (Polyvinyl choloride resin with hydroxyl groups)	27	Good color.
Vinylite VYLF (Copolymer of vinyl chloride and vinyl acetate)	25	Do.
Bakelite CKR 5254 (p phenyl phenol formaldehyde resin)	28	
Parlon S 10 (chlorinated rubber)	7	Resin only partly soluble. Results uncertain.
Orange shellac	25	Heavy color.
Polyviny formal	28	Excellent color.
½ second cellulose butyrate	25	Good color.
Polyisobutyl methacrylate	24	Do.
Beckamine P 196 (urea formaldehyde resin)	22	Do.
Epon 1001 (bisphenol epichlohydrin condensation product)	28	
Cumar Resin C (coumarone resin)	24	
Piccolyte 450S (coumarone indene resin)	31	Firm.
Vinsol	25	Dirty color.
Dymerex	28	
Polypale (polymerized rosin)	27	

The example indicates that in general, resins can be used as a general class as well as elastomers, to impregnate hide substance by the process of the invention.

Example VIII

Stock dehydrated as in Example IV, without the use of formaldehyde, was immersed in a solution consisting of

	Parts by weight
Vinsol resin (paraffin hydrocarbon insoluble residue from wood rosin)	20
Paraffin wax	10
45% formcel	5
Acetone	65

at 40° C. for 15 minutes. The temperature is not controlling; it may vary from room temperature to the boiling point.

The stock was rinsed with a mixture of 1 part by weight of the above solution to 4 of acetone for 10 minutes. It was then treated with water containing very small quantities of surfactant, tanning agents, dyes and acids, to complete the tannage.

While only a few examples of the technique for practicing the invention have been shown, it is obvious that the examples can be multiplied indefinitely and variations in the technique made without departing from the scope of the invention. It is only necessary that the stock be impregnated with formaldehyde and that the bulk of the formaldehyde be rinsed from the surface so that the stock be more heavily tanned with formaldehyde in the interior than in the outer layers. While the invention has been described as applicable to leather from cattle hides, it may obviously be applied to the preparation of other types of hides and skins provided the hides are thick enough, 1/16 inch or more, to produce leathers in which the difference between the interior and the exterior surfaces are noticeable.

What is claimed is:

1. A formaldehyde tanned leather of a thickness of at least 1/16 inch in which the interior of the leather contains substantially more formaldehyde combined with hide substance than do the outer layers and which leather produces a barrel-shaped cross section when a test section is immersed in water heated to the temperature at which the leather begins to shrink and is then withdrawn and permitted to dry.

2. A sole leather characterized by having a specific gravity of substantially under 1.0 and the excellent finishing characteristics of its grain surface, comprising cow hides of full thickness, the interior fibers of which are tanned with sufficient formaldehyde to render them resistant to compacting under pressure, and the grain fibers of which are reacted with so much less formaldehyde that grain crackiness is avoided.

3. A sole leather comprising cowhide, the interior fibers of which are tanned with sufficient formaldehyde to render the leather resistant to compacting under rolling pressure, and the grained surface of which contains substantially less reacted formaldehyde than the interior of the leather and is tanned with a hydrophilic vegetable tan which renders the surface easily wettable to facilitate finishing operations.

4. The method of tanning with formaldehyde which comprises treating hide substance with an impregnating solution consisting essentially of formaldehyde in an organic solvent containing insufficient water to cause tannage of the hide substance by the formaldehyde, treating the hide substance with an organic solvent for formaldehyde containing substantially less formaldehyde than in the impregnating solution to substantially reduce the formaldehyde content of the surface layers and then treating the hide substance with water to cause the formaldehyde to react with the hide substance, to produce a leather having substantially more formaldehyde combined with hide substance in the interior of the leather than in the outer layers thereof.

5. The method of tanning with formaldehyde which comprises treating porous untanned hide substance with an impregnating solution consisting essentially of formaldehyde in an organic solvent containing insufficient water to cause tannage of the hide substance by the formaldehyde, treating the wet hide substance with an organic solvent for formaldehyde containing substantially less formaldehyde than in the impregnating solution to substantially reduce the formaldehyde content of the surface layers and then reacting the formaldehyde with the hide substance, to produce a leather having substantially more formaldehyde combined with hide substance in the interior of the leather than in the outer layers thereof.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

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Seymour S. Kremen et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 45, for "Example II" read -- Example III --.

Signed and sealed this 17th day of October 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents

USCOMM-DC