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IMPREGNATED LEATHER AND MEANS OF PRODUCING

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This invention relates to the preparation of improved leathers such as sole leathers, and aims to provide new impregnated thicker leathers, which are characterized by having desirable properties derived from the impregnants without the undesirable properties hitherto obtained when leather is impregnated. The invention is also directed at novel methods for impregnating hide material which produce the desirable new leathers. In its most preferred aspect, this invention is directed to the production of tanned thicker leathers with unique properties, from hide material which has been dehydrated by replacement of the water therein with water-miscible readily volatile organic liquids such as the lower alkyl ketones and alcohols.

Conventionally, sole leather is prepared from full cattle hides (comprising about 23% hide collagen in the salt cured state) by a vegetable tanning process. The salt cured hides, as received by the tannery from the meat packers, are soaked to remove salt, blood etc. They are then lime treated to loosen the hair, which is next removed. A treatment with deliming salt and enzyme, known as bating, prepares the hides for tanning. At this stage of the process, the hides will contain about 25% by weight of hide collagen; the balance is principally water. The hides are then exposed to the tanning procedure, by being put into progressively stronger solutions of vegetable tanning agents such as quebracho, chestnut, oakgall etc. Since the tanning agent combines as it penetrates, and this tanning effect retards further penetration, complete tanning requires several weeks in common commercial practice, and to achieve penetration considerably more tanning agent must be picked up than the minimum necessary to chemically stabilize the collagen. It is estimated that as little as 4 to 6 pounds tannin would tan the 23 pounds of collagen present in 100 pounds of cured hides if properly distributed. Actually, about 30 pounds of tanning agent is present in the finished leather made from this 23 pounds of collagen. Most of this quantity of tanning agent is required to ensure complete penetration of tanning agent through the leather.

It was proposed as early as 1910 to shorten the tanning process by using the so-called "solvent tanning" method. In this method, the wet bated hides are treated with a low-boiling water-miscible solvent like methanol, ethanol, isopropanol or acetone; when the water has been removed by the solvent, the solvent is dried off to give a dehydrated hide which is essentially porous hide substance. Solvent dehydration is used to prevent the closing up of the pores which occurs when the water is removed directly. The open pored dehydrated hides are exposed to a non-aqueous solvent containing the tanning agent; when they have absorbed the necessary tanning agent, the liquid is removed, and the hides desolventized, depositing the tanning agent throughout the hides. If the hides are now exposed to water, tanning takes place very rapidly. No more tanning agent is necessary than is required to stabilize the collagen.

While the process seems simple in laboratory practice, it has not been commercialized on any substantial scale for a number of reasons. Because of either the thickness or area of the pieces, it has been difficult to effect dehydration economically, and uniform tannage has been

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difficult to obtain on large pieces. Finally, it has been difficult even in laboratory operations to keep the leather sufficiently plump during finishing, so that the finished leather lacks body. The problems of economical dehydration and uniform tannage have been overcome, using the processes described in our copending application, Serial No. 535,755, filed September 21, 1955, now U.S. Patent No. 2,917,833. However, attempts to get plumpness and body by the use of impregnants such as resin have produced material of poor quality, which finish poorly and have cracky grains.

It is an object of the present invention to impregnate previously prepared leather with resin in such fashion that the finishing qualities of the previously prepared leather are not impaired, and to impregnate solvent dehydrated hides with resin so that the finishing operations are substantially reduced as compared with ordinary leather.

It is a further object of this invention to produce leathers which have desirable plumpness, are lighter in weight than conventional leather, as well as to produce leathers which are more waterproof than conventional leather, and possess added abrasion resistance, controlled firmness and good cutting properties.

In accordance with the present invention, porous hide material, either before or after tanning, is impregnated with a solution of a non-tanning impregnant; the impregnated hide material is then rinsed with a solvent for the impregnant to reduce the concentration of the impregnant in the outer layers of the hide material; and the impregnant solvent is then extracted with a material which dissolves the impregnant solvent but not the impregnant, so that the impregnant is precipitated in the hide material in substantially greater concentration at the center of the material than at the outer layers. The hide material is preferably tanned before or during the process, so that an impregnated leather results directly, or it may be tanned after setting the impregnant.

The resultant product is an impregnated leather which has the desirable characteristics imparted to it by the central layer of impregnant, but has the excellent finishing characteristics of non-impregnated leather, due to the relative freedom from impregnant of the surface layers.

The process and product of this invention differ markedly from prior art impregnated leather. Impregnation has heretofore been accomplished by immersing the hide material before or after tanning, in a solution of impregnant in a volatile solvent, and heating the hide material to drive off the solvent. We have found that this procedure causes a migration of the impregnant to the surface layers and produces leathers with less impregnant in the interior than at the surfaces. Rinsing of the surface prior to evaporation is of little help in solving the problem; migration and excessive impregnant concentration at the surface still result. It is only when the impregnant is precipitated in accordance with this invention, after rinsing excess impregnant from the surface layers, that the desirable results of the instant invention are obtained.

In carrying out the invention with ordinary tanned leathers in the unfinished state, improved abrasion resistance, firmness and resistance to water uptake can be obtained with materials such as resins, waxes, oils, plasticizers, cellulose derivatives and elastomers such as natural and synthetic rubbers. After treatment, the leathers are finished in conventional fashion.

Even better results are obtainable with untanned hide substance obtained by dehydrating wet hides with solvents such as acetone and the lower alcohols; one process which may be used is described and claimed in the copending Kremen et al. application Serial No. 535,755, filed September 21, 1955. Such dried hides may be im-

mersed in solutions, preferably in acetone or a lower alcohol, containing both an impregnant, such as described in the preceding paragraph, and a tanning agent.

In the next step, the hides are rinsed, preferably by immersion, with a solvent for the impregnant, preferably the same solvent used for impregnation, either with no impregnant or a low concentration of impregnant. In ordinary plant operations, the rinsing solvent will build up to a relatively low impregnant content rapidly, and then will stay at that figure. The maximum impregnant content permissible in the rinse is a fraction of the amount permissible in the outer layers of the finished leather. In general, amounts as high as 20% have little or no effect; higher amounts can be tolerated with many impregnants.

In the third step in the process, the hides are again treated, preferably by immersion, with an extracting solvent which dissolves the impregnant solvent but precipitates the impregnant. This extracting solvent is preferably water, which removes the solvent, acts to set the tanning agent and precipitates the impregnant.

Since the impregnant will not migrate in the presence of a non-solvent, the extraction solvent may be removed by evaporation, or may itself be extracted with a volatile extraction solvent which is a non-solvent for the impregnant, preferably by water to complete the tanning.

The resultant leather now has a concentration of impregnant in the interior, and outer grain and flesh surfaces relatively free of impregnant, and with substantially less tanning agent than in conventional leather. As a result, finishing operations are substantially eased, and improved finish can be obtained with less effort, the body, firmness, plumpness and strength being provided by the impregnants in the body of the leather.

Typically, a standard tanned sole leather will contain, per 100 pounds of hide substances, about 120 pounds of tannin and 60 to 80 pounds of finishing material; the resultant leather will have a specific gravity of about 1.0 or more. When the instant process is used with solvent dehydrated hides, the same 100 pounds of hide substance will contain less than half as much tannin as hide substance, preferably about one-third as much, and from 10 to 60 pounds of impregnant, plus less finishing material than standard leather. By proper choice of impregnants, it can have approximately the same volume as standard leather, and yet have a specific gravity as low as 0.65.

The invention cannot be applied to the production of very thin leathers, because the rinsing operation removes material down to a depth of about $\frac{1}{8}$ inch (called an "iron" in the leather trade). Hence, in a piece only $\frac{1}{4}$ inch in thickness, a rinse will remove substantially all of the impregnant. For the invention to have practical utility, the unrinsed layer should be at least almost equal to the rinsed layer in thickness; hence, the invention requires that the hide substance being treated have a thickness of about $\frac{1}{16}$ inch (3 irons).

The following typical examples of the invention are supplied by way of example and not as a limitation on the invention, which can be practiced with a wide variety of other materials, and in other manners, as defined in the claims.

Example I.—Pretanned leathers

Three samples of leather were selected. One was a quebracho tanned sole leather $\frac{3}{8}$ inch (9 irons) thick; one was a chrome tanned upper leather $\frac{1}{2}$ inch (4 irons) thick; and the third was a chrome-quebracho tanned sole leather $\frac{3}{8}$ to $\frac{7}{8}$ inch (6 to 7 irons) thick. These were all unfinished, rough dried leathers, so that they were still porous.

A solution was prepared consisting of:

	Pounds
Dymerex resin (dimerized rosin)	20
Paraffin wax (M.P. 50° C.)	10
99% isopropanol, 120° F.	70

The leathers were immersed in the solution, at 120° F., for 20 minutes. The pieces were drained, and then immersed for 10 minutes in a solution consisting of:

	Parts by weight
Above resin wax solution	1
99% isopropanol at 120° F.	4

After 10 minutes, the pieces were drained, immersed for 30 minutes in cold water, drained and dried.

The resulting leathers all showed greatly reduced water uptake, increased abrasion resistance and better firmness than the original leather. They finished comparably to the untreated leathers.

On splitting the pieces, it was observed that the resin and wax were concentrated in the center of the pieces away from the surfaces.

Essentially identical results were obtained by substituting polymerized rosin—Polypale—for the Dymerex. When Vinsol resin (paraffin hydrocarbon insoluble residue obtained in the purification of wood rosin) was used, properties were identical, except that the leather had a definite yellowish color.

Example II.—Pretanned leathers with non-aqueous precipitation

The three leathers of Example I were again used, and immersed for 15 minutes in a solution consisting of:

	Pounds
Polybutene (medium mol weight)	20
Methylene chloride	80

at room temperature.

In one group of tests, the three impregnated leathers were rinsed by a 15 minute immersion in a 4% solution of polybutene in methylene chloride; in a second group of tests, the leathers were rinsed by a 10 minute immersion in pure methylene chloride. Results were comparable.

The methylene chloride was removed by immersion of the samples in acetone for two hours. One of the samples was treated with isopropanol, with similar results. The samples were removed from the extracting solvents, drained and the acetone or isopropanol removed by evaporation.

The resultant leathers were equally satisfactory during finishing, and had the same appearance as the original leathers. The leathers exhibited improved flexibility, water resistance and abrasion resistance.

Example III.—Impregnation with butyl rubber

The vegetable tanned leather of Examples I and II was treated as in Example II, with a 20% solution of butyl rubber in methylene chloride, rinsed with a 4% butyl rubber solution in methylene chloride and the methylene chloride extracted with isopropanol. The resultant leather was essentially similar to that obtained in Example II from the same leather.

Example IV.—Untanned hide substance

An unsplit cow hide was dehydrated by extraction with acetone, and the acetone evaporated off under conditions that prevented wrinkling of the hide as described in application Serial No. 535,755 filed September 21, 1955. It was immersed in a solution comprising:

	Parts by weight
Raw quebracho (20% water—80% solids—about 65% tannin)	5
Dymerex resin (dimerized rosin)	20
Paraffin wax (M.P. 50° C.)	10
Formaldehyde (added as 40% formalin)	2
Water (from the formalin)	3
Acetone	60

at 120° F., and allowed to stay for 15 minutes to ensure complete impregnation.

The hide was drained and immersed in a solution at 120° F., comprising:

Parts by weight

Quebracho extract as above	5
Dymerex resin	4
Paraffin wax as above	2
40% formalin	1
Acetone	88

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

The resultant tanned leather was about 9 to 10 irons thick, had a high abrasion resistance, low water uptake, very low specific gravity (0.65), excellent chemical and thermal stability, resistance to perspiration, and a very natural appearing surface which responded so readily to finishing operations that a desirable finish was obtained with far less labor and material than for conventional quebracho tanned leather.

In this case, the quebracho extract, which does part of the tanning, was purposely kept at the same level on the surface as on the interior. The formaldehyde which imparts resistance to compacting during the finishing operation, was reduced by rinsing to assure against crackiness in the grain. This special utility of formaldehyde is described and claimed in the copending Kremen and Southwood application Serial No. 729,254, filed April 18, 1958.

Example V

Example IV was repeated, except that the 5 parts of formalin in the impregnation solution was replaced by 5 parts of quebracho extract, and the formalin in the rinse solution was replaced by acetone. The resultant leather was slightly less firm than the leather of Example IV, but otherwise had similar properties.

Example VI

A series of resins was tested on pieces of dehydrated hide similar to that used in Example IV. 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
1/4 second microcellulose	15	Very pale color.
Manila gum MA	24	
Clorafin 42-S (chlorinated paraffin 42%)	22	Leather softer than Dymerex.
Vinylite VAGH (Polyvinyl chloride 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.
Polyvinyl formal	28	Excellent color.
1/2 second cellulose butyrate	25	Good color.
Polyisobutyl methacrylate	24	Do.
Beckamine P 196 (urea formaldehyde resin)	22	Do.
Epon 1001 (bisphenol epichlorohydrin condensation product)	28	
Cumar Resin C (coumarone resin)	24	
Piccolyte 450 S (coumarone indene resin)	31	Firm.
Vinsol	25	Dirty color.
Dymerex	25	
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 VII

A hide similar to that used in Example IV was split to produce a grain split about 4 1/2 irons thick. It was immersed for 10 minutes in a solution at 120° C., containing

Quebracho extract (as in Example IV)	8
Dymerex	8
Paraffin wax (50° C. melting point)	5
Paraffin oil	3
Distilled animal fatty acids (50% oleic-50% saturated acids)	3
Methyl formcel (55% formaldehyde-45% methanol)	5
Acetone	68

The impregnated split hide was drained, and rinsed with a solution of

Quebracho extract	1.6
Dymerex resin	1.6
Paraffin wax	1.0
Paraffin oil	0.6
Distilled animal fatty acids as above	0.6
Methyl formcel	1.0
Acetone	93.6

by immersion for 10 minutes at 120° F. The rinsed split hide was drained, immersed in water for an hour, drained and dried. It was finished in the conventional manner used for upper leathers, and gave a satisfactory finished upper with less than normal labor. The leather had better water resistance than conventional upper leathers.

Example VIII

Example IV 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 acid mixture)	2.5
Acetone	62.5

and the rinse solution consisted of 20% of this impregnating solution, 80% acetone. After the water immersion, however, 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 IV, 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 water-impervious interior makes the leather proof to penetration by water.

Tan liquors other than the specific quebracho extract shown can be used to give the desired surface appearance and finishing characteristics.

Example IX

A series of sole leathers was prepared from an un-

split cow hide like that described in Example IV, with three different impregnating solutions, as follows:

	A	B	C
Quebracho solution.....	0	8	10
Dymere resin.....	24	20	16
Paraffin wax—M.P. 50° C.....	8	6	6
Distilled fatty acids of Example VII.....	3	3	3
Formol.....	5	3	3
Acetone.....	60	60	63

In each case, the dehydrated hide was immersed in the impregnant for 15 minutes at 120° F., drained and immersed in the original bath diluted with four times its weight of acetone, for 10 minutes at 120° F., drained, immersed in water for several hours and dried.

All the leathers finished more readily, and gave lighter, more water-resistant leathers than conventional quebracho tanned leather; abrasion resistance was likewise improved.

Leather A had the desired stiffness desired by cobblers in finders leather; leather B had the feel and stiffness appropriate for men's shoe manufacture; and leather C was softer, and met the requirements for ladies' shoe soles.

These leathers may be advantageously treated with a vegetable tan after water immersion, before drying, as in Example VIII.

Example X

An unsplit cow hide, dehydrated by extraction with acetone, was impregnated with a solution containing:

	Parts by weight
Quebracho extract as in Example IV.....	15
Vinsol resin.....	16
Paraffin wax, M.P. 50° C.....	5
Distilled animal fatty acids as in Example VII.....	3
Acetone.....	61

The dehydrated hide was immersed in the impregnant for fifteen minutes at 120° F., drained and immersed in a solution of 15 parts by weight quebracho extract and 85 parts by weight of acetone for ten minutes at 120° F., drained, immersed in water for several hours and dried.

This leather contained about 30% of tannin, based on hide substance. It is somewhat darker in color than standard sole leather, more water resistant, much lighter in weight. As compared with the leathers of Example IX, it compacts slightly more.

Obviously, the above examples can be multiplied indefinitely. The process opens up to the leather manufacturer the use of any impregnant which is soluble in any solvent, since the solvents can in turn be extracted with agents which will precipitate the impregnant while removing the solvent therefor. Obviously, the solvents used should be inexpensive and preferably of low boiling point, so that they can be economically recovered. And most advantageously water-insoluble impregnants dissolved in water-miscible solvents are the most economic materials to use in the process, since this reduces the solvent recovery problem to a single solvent, and permits tanning to take place during the solvent removal impregnant precipitation step.

Typical of the impregnants which may be used are the natural and synthetic resins, cellulose derivatives, soluble waxes and natural and synthetic rubbers in soluble form; unpolymerized or partially polymerized materials which can be converted in the leather before the drying operations so as not to migrate, may also obviously be used. The properties of these impregnants may be modified in known manner by adding plasticizing agents, stabilizers, lubricating agents such as waxes and the like, to improve stability, waterproofness, flexibility and workability of the finished leather.

While the invention has been described as applicable to the preparation of leather from cattle hides, it may obviously be applied to the preparation of leather gen-

erally where the skins are at least about $\frac{1}{16}$ inch in thickness.

What is claimed is:

1. Leather characterized by the fact that it contains water insoluble impregnants other than hide substance and tanning agents therefor, the impregnants being substantially less concentrated in the surface layers than at the center.

2. Leather about $\frac{1}{16}$ inch or more in thickness and containing water insoluble impregnants other than hide substance and tanning agents therefor, the impregnants being substantially less concentrated in the surface layers of the leather than at the center thereof.

3. Leather of a thickness of at least $\frac{1}{16}$ inch containing a water insoluble non-tanning resinous impregnant, the impregnant being substantially less concentrated in the surface layers than at the center.

4. A leather tanned with vegetable tannins and containing in addition a water insoluble non-tanning impregnant, the leather being characterized by containing less than half as much vegetable tannin as hide substance, and a lower concentration of non-tanning impregnant in the surface layers than at the center.

5. A leather tanned with vegetable tannins and formaldehyde, and containing in addition a water insoluble non-tanning impregnant, the leather being characterized by containing less than half as much vegetable tannin as hide substance, and a lower concentration of non-tanning impregnant and formaldehyde in the surface layers than at the center.

6. A leather tanned with vegetable tannins and formaldehyde, and containing in addition a water insoluble non-tanning resinous impregnant, the leather being characterized by containing less than half as much vegetable tannin as hide substance, and a lower concentration of non-tanning impregnant and formaldehyde in the surface layers than at the center.

7. The method of producing impregnated hide substance which comprises impregnating porous hide substance with a solution of a water insoluble impregnant which is not a tanning agent for the hide substance, rinsing the wet hide substance with a solvent for the impregnant which contains no more than a small amount of said impregnant to reduce the concentration of impregnant in the outer layers of the hide substance, precipitating the impregnant in the hide substance by treatment with an extraction medium which is a solvent for the impregnating solvent and a non-solvent for the impregnant, and then removing the extraction medium to leave the impregnant in the hide substance in greater concentration in the center than in the outer layers.

8. The method of producing impregnated hide substance which comprises impregnating porous hide substance with a solution of a water insoluble non-tanning resinous impregnant in a solvent therefor, rinsing the wet hide substance with a solvent for the impregnant which contains no more than a small amount of said impregnant to reduce the concentration of impregnant in the outer layers of the hide substance, precipitating the impregnant in the hide substance by treatment with an extraction medium which is a solvent for the impregnating solvent and a non-solvent for the impregnant, and then removing the extraction medium to leave the impregnant in the hide substance in greater concentration in the center than in the outer layers.

9. The method of producing impregnated leather which comprises impregnating tanned unfinished leather with a solution of a water insoluble non-tanning resinous impregnant in a solvent therefor, rinsing the wet leather with a solvent for the impregnant which contains no more than a small amount of said impregnant to reduce the amount of the impregnant in the outer layers of the leather, precipitating the impregnant in the leather by treatment with an extraction medium which is a solvent for the impregnating solvent and a non-solvent for the

impregnant, and then removing the extraction medium to leave the impregnant in the leather in greater concentration in the center than in the outer layers.

10. The method of producing impregnated leather from dried porous untanned hide substance which comprises impregnating the hide substance with a solution of a water insoluble non-tanning resinous impregnant and a tanning agent in a non-aqueous solvent therefor, rinsing the wet hide substance with a non-aqueous solvent for the resinous impregnant which contains no more than a small amount of said impregnant to reduce the concentration of the impregnant in the outer layers of the hide substance, precipitating the impregnant in the hide substance by treatment with an extraction medium which is a solvent for the impregnant solvent and a non-solvent for the impregnant and then removing the extraction medium to leave the impregnant in the hide substance in greater concentration in the center than in the outer layers.

11. The method of producing impregnated leather which comprises impregnating a dried porous hide substance with a solution of a water insoluble non-tanning resinous impregnant and a tanning agent in a non-aqueous solvent therefor, rinsing the wet hide substance with a water-miscible solvent for the impregnant which contains no more than a small amount of said impregnant to reduce the concentration of impregnant in the outer layers of the hide substance, treating the hide substance with water to precipitate the impregnant, set the tanning agent and remove the solvent from the hide substance, and then removing the water to leave the impregnant in the hide substance in greater concentration in the center than in the outer layers.

12. The method of claim 11, in which the non-aqueous solvent and the water-miscible solvent for said impregnant each comprise the same solubilizing substance.

13. The method of producing sole leather which comprises impregnating a dried porous untanned cow hide with a solution containing vegetable tannin, water insoluble resin and formaldehyde in a water miscible organic solvent for the vegetable tannin, resin and formaldehyde, rinsing the wet hide substance with a water miscible organic solvent which contains no more than a small amount of resin and formaldehyde to reduce their concentration in the outer layers of the hide, precipitating the resin, and simultaneously removing the organic solvent and causing the tannin and formaldehyde to react with the hide to produce a tanned leather, by treatment

with water, and then removing the water leaving a tanned leather in which the resin and formaldehyde are in greater concentration in the center of the leather than in the outer layers.

14. The method of claim 13, in which the organic solvent is acetone.

15. A sole leather having a specific gravity of substantially under 1.0, the interior fibers of which are impregnated with sufficient resinous impregnation to render the leather water resistant and which are tanned with sufficient formaldehyde to render them resistant to compacting under pressure, and the grain fibers of which contain substantially lesser concentrations of said resinous impregnation and formaldehyde.

16. The method of producing impregnated leather from porous hide substance which comprises impregnating the porous hide substance with a solution of a resinous impregnant and formaldehyde in an organic solvent therefor, rinsing the wet hide substance with an organic solvent for the resinous impregnant and the formaldehyde which contains no more than a small amount of the resinous impregnant and the formaldehyde to reduce the concentration of the resinous impregnant and the formaldehyde in the outer layers of the porous hide substance, treating the hide substance with water to precipitate the resinous impregnant, set the formaldehyde and remove the impregnant solvent from the porous hide substance to produce a leather having substantially more resinous impregnant and formaldehyde combined with hide substance in the interior of the leather than in the outer layers thereof.

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