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2,995,415

TANNING WITH LIGNIN SULFONIC ACID-CHROMIUM COMPOUND REACTION PRODUCT

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 No Drawing. Filed May 4, 1960, Ser. No. 26,675
 12 Claims. (Cl. 8-94.26)

This invention relates to a new and improved process for the tanning of leather and more particularly relates to a new and improved leather tanning process which utilizes a chromium-containing tanning composition.

This application is a continuation-in-part of our co-pending application Serial No. 650,825, filed April 5, 1957, now abandoned.

At the present time, two recognized types of tanning procedures have been accepted and widely-practiced in the leather industry. These are the so-called "vegetable" tanning wherein the conversion of the hide to leather is accomplished with aqueous tanning solutions, extracted from materials of vegetable origin, such as finely-ground oak or hemlock bark or the like, and the so-called "chrome" tanning which utilizes various reducible salts of chromium, notably alkali metal bichromates, and especially sodium bichromate, to effect the conversion of the hides to leather.

Each of these tanning techniques has several advantages which has justified its continued use despite other somewhat serious disadvantages, which at the present time, have not been completely overcome. For example, vegetable tanning produces leather and particularly sole leather of an excellent color, having wear properties and waterproofness which are generally quite satisfactory. However, vegetable tanning is an extremely slow process and hence, despite the advantage of producing a so-called "full" leather of good color, the slowness of vegetable tanning has precluded its use in many applications where it otherwise would be highly desirable.

On the other hand, the outstanding advantage of chrome tanning is the speed with which the tanning is effected. Moreover, chrome tanned leather exhibits good wear and abrasion resistant properties. However, the principal disadvantages of conventionally chrome tanned leather, especially when used as sole leather, are that it is susceptible to distortion and at times is slippery on wet surfaces.

In an effort to overcome the recognized disadvantages of vegetable and chrome tanning, prior workers in the art have proposed several variations in tanning procedure. For example, it has been suggested that leather first be tanned with a vegetable tanning material and then retanned with a cationic chromium-containing tanning composition, i.e., the conventional type of chrome tanning composition. Advantages of such a procedure are that a higher shrinkage temperature is obtained, together with increased abrasion resistance, especially in sole leather so prepared. However, it has been found that leather thus-produced frequently has a poor color. Moreover, since such a procedure involves additional treatment, inevitably there is an increase in cost involved. In addition, the extremely slow vegetable tanning process, used as a first step, still is encountered.

Alternatively, prior workers in the art also have proposed first to chrome tan leather and then to use a vegetable tanning composition as a retan. However, this technique has not been found to be the complete answer to the problem either, because a heavy vegetable tan frequently is required to obtain a satisfactory leather color. Inasmuch, as the desired wear properties of the leather generally decrease with an increase in the amount of vegetable tanning effected, this procedure has resulted in a leather, and particularly sole leather, having poor wear characteristics.

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Accordingly, it will be appreciated that up to the present time no completely satisfactory tanning technique has been available for the tanning of leather, particularly leather destined for application as sole leather.

It is, therefore, the principal object of the present invention to provide an improved leather, especially sole leather, characterized by a maximum of the desirable properties of vegetable-tanned leather as well as those of chrome-tanned leather, while minimizing the disadvantages of both tanning techniques.

A further object of the present invention is to provide a new and improved tanning process by means of which this improved leather can be produced.

These and other objects of the present invention will become apparent to those skilled in the art from the description of the invention which follows.

The present invention envisions a tanning process which utilizes a predominantly non-ionic, chromium-containing composition to produce a leather characterized by good color, solidity, fullness, workability, and excellent abrasion and water resistance. Such tanning composition is obtained by chemically reacting lignin sulfonic acid with at least sufficient of a hexavalent chromium compound to produce a predominantly non-ionic, chromium-containing material.

In preparing this non-ionic, chromium-containing composition, the amount of hexavalent chromium compound employed must not be less than about 25% by weight of the lignin sulfonic acid, expressed in terms of lignin solids used in preparing the lignin sulfonic acid. Moreover, it has been found that the amount of hexavalent chromium compound employed should not exceed about 50% by weight of the lignin sulfonic acid, again expressed in terms of lignin solids. It will, of course, be understood that the hexavalent chromium compound may be chromic acid or an alkali metal bichromate, the term "alkali metal" referring to sodium, potassium, lithium, rubidium and cesium. However, because of its low cost and ready availability, the preferred hexavalent chromium compounds are the alkali metal bichromates, of which sodium bichromate is the most preferred. For this reason, hereinafter particular reference will be made to sodium bichromate as the source of hexavalent chromium.

The expression "lignin sulfonic acid" as used throughout the specification and claims is intended to refer to lignin sulfonic acid obtained from neutralized sulfite waste liquors. In practice, these liquors, formed as a by-product from the cooking of wood fibers in the paper industry, are generally neutralized with calcium or magnesium salts and the resulting liquors used as such or spray dried to obtain a crude water-soluble lignin sulfonate, generally calcium sulfonates, or as termed herein, "lignin solids." One commercially available product of this type is termed "Goulac." The water-soluble lignin solids can be dissolved in water and acidified prior to use in the practice of this invention, or, if desired, may be formed in situ during the preparation of the composition embodying the present invention.

A typical commercially available Goulac (lignin solids) has the following analysis:

	Percent by wgt.
Water -----	2.32
Ash -----	10.50
Fe -----	0.021
CaO -----	4.51
MgO -----	3.00
Solids -----	97.68
Nontans (i.e., sugars, salts, and the like)-----	54.46
Tans -----	43.22
pH -----	6.60

The term "non-ionic" as applied to chromium throughout the specification and claims is intended to refer to chromium, the major part of which has substantially no electrical charge as detectable by ion exchange techniques. Thus, the chromium-containing tanning composition used in the present method comprises chromium in a non-ionic form as a major ingredient, i.e., an amount of at least 50% by weight. Attention is now directed more specifically to the various aspects of the invention, notably the tanning composition, its preparation and use in tanning.

The tanning composition of this invention comprises the chemical reaction product of a major proportion of lignin sulfonic acid, e.g., prepared by the acidification of dissolved lignin solids, with a minor proportion of a hexavalent chromium compound, e.g., an alkali metal bichromate, preferably sodium bichromate, in the amount of at least 25% by weight of the lignin solids, which amount is sufficient to produce a predominantly non-ionic, chromium-containing reaction product in which the content of non-ionic chromium is at least 50% by weight. This composition is desirably partially neutralized to an acid pH within the range from about 3.0 to 4.5, 4.0 being preferred.

The proportion of the reactants which are employed is critical, in that the minimum amount of the hexavalent chromium compound, especially sodium bichromate, which is to be used, must be at least 25% by weight of the lignin solids, which amount is sufficient so that the reducible hexavalent chromium present is converted in the reaction product to a predominantly non-ionic form in the amount of at least 50% by weight. Moreover, the maximum amount of hexavalent chromium compound to be employed is found to be about 50% by weight of the lignin solids inasmuch as when greater amounts are used, the product does not contain a predominant proportion of non-ionic chromium. Additionally, if an amount of sodium bichromate greater than 50% by weight of the lignin solids is used, the reaction mixture gels and becomes virtually impossible to work with.

Preferably, the reaction product is partially neutralized to reduce its otherwise extremely low pH to a higher, but still acid pH of about 3.0 to 4.5, as pointed out hereinabove. The reaction product may be used as such, without further treatment, as a solution or may be concentrated or dried. Preferably, the reaction product is spray dried at an elevated temperature.

In practice, the desired amount of water-soluble lignin solids is dissolved in water, with agitation, and the resultant solution is acidified using a mineral acid, such as hydrochloric or sulfuric acid, the latter of which is preferred. The amount of sulfuric acid used is preferably about 35% by weight of the lignin solids. Alternatively to in situ formation of the lignin sulfonic acid, an aqueous solution of lignin sulfonic acid may be employed. In either case, to the resultant lignin sulfonic acid solution with continuous agitation, is added an aqueous solution of a hexavalent chromium compound. Preferably an alkali metal bichromate and especially sodium bichromate, typically as a 50% by weight solution. The rate of addition of this solution is such that in combination with the agitation, the formation of lumps or gel particles is avoided. Typically, in a commercial operation, the addition time is at least one hour, 1-2 hours being preferred. This solution is added in the amount of at least 25% by weight as sodium bichromate, of the lignin solids, and not in excess of 50% by weight as sodium bichromate, of the lignin solids. Continuous agitation is effected until the chemical reaction and dissolution are complete.

The resultant solution, generally having a pH of about 2, may be used as such in those applications wherein extremely acid material is not objectionable. However, it generally is desirable and is preferred, partially to neutralize this solution by addition of alkali, e.g., sodium

hydroxide, sodium bicarbonate or other alkaline substance, to raise the pH to a value of about 3.0 to 4.5, preferably about 4.0. Generally, the sodium hydroxide is added in an amount of about 11% by weight of the lignin solids used.

The partially neutralized solution then may be used as such or, depending upon the application, may be concentrated or dried. An especially advantageous treatment constitutes spray drying of the material at an elevated temperature. Typical spray drying conditions involve adjusting the desiccating chamber of the drier so as to provide an air inlet temperature of about 300° to 500° F., preferably about 400° F., and an air outlet temperature of about 200° to 250° F., preferably 210° to 230° F.

The practice of the present invention in respect to tanning of leather involves subjecting the hides to be tanned, after conventional soaking or washing, fleshing, dehairing, bating and pickling, to an aqueous solution of a predominantly non-ionic, chromium-containing reaction product obtained by chemically reacting lignin sulfonic acid with the hexavalent chromium compound in the amount of at least 25% by weight of the lignin solids in the lignin sulfonic acid, at an elevated temperature for a period of time sufficient to effect the desired tanning. In many instances, it is advantageous to soak the stock immediately prior to tanning, in an aqueous solution of an alkali metal halide, notably sodium chloride, e.g., in a 1-15% by weight sodium chloride solution.

In the carrying out of tanning in accordance with this invention, it is desirable to maintain the pH of the tanning solution within the range of about 4.0 to 6.0, 5.0 being the specifically preferred pH. Additionally, tanning is preferably carried out at temperatures above ordinary room temperature, e.g., from about 90° to 110° F. and preferably about 100° F., although it will be appreciated that in some applications higher tanning temperatures, i.e., to about 130° F. may be used, the upper temperature limit generally being dictated by the quality of leather which is required. Conversely, a minimum practicable tanning solution temperature generally is about 85° F. but is, of course, dictated by the time available for tanning.

The time required for tanning in accordance with the practice of the present invention depends on a large number of variables, including the type of stock, thickness, prior treatments, and effect desired, so that a satisfactory "shrink temperature" can be obtained. It is understood that by "shrink temperature" is meant the elevated temperature at which shrinkage of the leather in water, or a glycerine-water mixture, first is observed, which temperature is used as a measure of tanning effectiveness, a shrink temperature of 200° F. or higher indicating a satisfactorily tanned leather. As a general guide, however, it is desirable to subject the hides to the tanning solution of the present invention for a period of at least 1 hour, typically 1-10 hours and preferably about 8 hours at the temperatures indicated hereinabove. In this manner, shrink temperatures of 200° F. or higher are readily obtained.

The concentration of the tanning solutions may also be varied, it generally being desired to use a tanning solution containing about 20-35% solids, 30% solids being especially preferred, based on the weight of the wet hides to be tanned. Moreover, the amount of the tanning solution used is generally about 60-120% by weight of the wet hides to be tanned. Following this tanning procedure, the thus-tanned hide may, if desired, advantageously be retained with a vegetable tanning material, a conventional chrome-tanning material or, with the predominantly nonionic tanning composition of the present invention or a combination of chrome and vegetable retans. Alternatively, the leather may be used without further treatment or, it may, be fat liquored and/or

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waterproofed prior to usage with or without any of the aforementioned retannings.

In order that those skilled in the art may better understand the method of the present invention and the manner in which it may be practiced, the following specific examples are given. It is to be understood, of course, that the examples are not to be constituted as limiting the invention but are intended merely to be illustrative thereof.

EXAMPLE 1

One hundred lbs. of Goulac (lignin solids) is dissolved in 250 lbs. (30 gallons) of water and 35 lbs. of 95% by weight sulfuric acid is added thereto and the resulting mass is agitated for 1 hour, during which time SO₂ fumes are evolved. Twenty-five lbs. of Na₂Cr₂O₇·2H₂O as a 50% by weight solution is then added slowly with continuous and vigorous agitation to avoid formation of any chrome-lignin gel lumps. After all the bichromate solution is added, the mass is agitated for 2 hours after which time 5.5 lbs. of sodium hydroxide is added, as a 25% solution, with continuing vigorous agitation. The resultant mixture is allowed to stand overnight, after which time another 5.5 lbs. of sodium hydroxide, as a 25% solution, is added with vigorous agitation and sufficient water is then added to make a total volume of 50 gallons. The pH of the resultant liquid tanning solution is 4.0. Chemical analysis of the liquid tan so prepared is as follows:

	Percent by weight
Solids	28.6
Cr ₂ O ₃	2.52
Anionic chromium	23.9
Non-ionic chromium	70.7
Cationic chromium	5.4

This material can be employed either as a liquid or spray dried, advantageously with the desiccating chamber of the dryer adjusted so as to provide an inlet air temperature of about 400° F. and an outlet air temperature of about 210° to 230° F., during the drying operation.

EXAMPLE 2

Stock, consisting of pickled steer hides, is floated in a tanning drum in a 10% sodium chloride solution for a period of 10 minutes, the amount of sodium chloride solution being equal to the weight of the stock. To the thus-treated stock is added the liquid tan prepared in Example 1 in the amount of 50% by weight of the stock. Tanning is carried out for 2 hours at 100° F. after which time an additional quantity of the liquid tan in the amount of 50% by weight of the stock is added and tanning is continued for a total of 4 hours. Thereafter, a 5% aqueous solution of sodium bicarbonate is added to the tanning drum in the amount of 3% by weight of the stock so as to raise the pH of the tanning solution to 5.0. Tanning is continued for a total tanning time of 8 hours, after which time a shrink temperature of 200° F. is obtained. The stock is then horsed up overnight and washed with water until a clear effluent is obtained. The thus-tanned leather may be employed as such or may be subjected to further treatment as indicated in the following examples.

EXAMPLE 3

The leather prepared in accordance with Example 2 is floated at 100° F. and retanned with 5% Tanolin R, a commercial one-bath tannage produced by the Diamond Alkali Company and comprising chromium sulfate having the following analysis:

Cr ₂ O ₃	Al ₂ O ₃	Basicity
Percent 23.5	Percent 1.6	Percent 33-35

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basicity being defined as the percent of total chromium present which is linked to hydroxyl groups. Using this procedure, an excellent leather is obtained.

EXAMPLE 4

Stock produced in accordance with Example 2 is retanned with a vegetable tan. 2 to 4% of a fat liquor is added to the vegetable tan after ½ hour of the tanning run. Using this procedure an excellent leather is obtained.

EXAMPLE 5

The leather produced in accordance with Examples 2 and 3 is fat liquored using a 2% solution of Neutrolene 7A (a cationic-non-ionic animal type fat liquor) in an amount equal to the weight of the stock to be fat liquored, at 120° F. Using this procedure, a complete take up of the fat liquor by the stock is effected. Advantageous fat liquoring can also be effected using a fat liquor comprising raw neat's-foot oil and an emulsifier therefor such as the various cationic emulsifying materials.

Leather treated in accordance with the present invention, if desired, may be rendered even more water-repellant by further treatment with a water repellent, such as silicone resins, e.g., Dow Corning Silicone 1109 or "Quilon" (stearato chrome complex in isopropyl alcohol).

EXAMPLE 6

To illustrate the excellent properties of leather obtained by the practice of the present invention, leather tanned in accordance with the procedure set forth in Example 2 is subjected to water absorption tests in which a weighed specimen of leather is immersed in distilled water for periods of 30 minutes and 120 minutes, any gain in weight being calculated as a percentage gain of the conditioned weight of the sample. Additionally, the leather is subjected to an abrasion test using a U.S. Bureau of Standards abrasion testing machine in which the wear loss in thickness is measured against a standard sole leather and the results reported in the number of cycles necessary to wear away 0.05 inch and 0.10 inch using 1 x 1 inch test pieces with 3M No. 2½ garnet paper. In these tests, leather tanned using the chromium tanning composition prepared in accordance with Example 1 is compared to leather tanned with a composition prepared in the same manner with the exception that the amount of sodium bichromate used is only 20% by weight of the lignin solids rather than 25% by weight. Additionally, two tests are made using leather tanned with a tanning composition prepared by reacting the lignin sulfonic acid with 35% and 40% sodium bichromate by weight of the lignin solids. The results of these tests are as follows:

Test No.	Sodium Bichromate/ Lignin Solids Ratio	Abrasion Cycles		Percent Water Absorption	
		0.05 In.	0.10 In.	0.5 hours	2.0 hours
1	0.20	2,167	2,983	16.1	28.8
	0.25	2,883	5,273	12.3	24.1
2	0.20	742	1,067	29.6	45.3
	0.25	658	1,033	10.3	18.2
3	0.25	1,858	2,658	7.2	12.0
	0.20	425	700	17.8	34.4
4	0.25	538	790	13.7	27.9
	0.20	1,062	1,685		
5	0.25	1,700	2,617		
	0.20	2,017	3,033	21.6	31.8
6	0.25	2,592	4,558	19.3	32.0
	0.20	942	1,217	31.2	52.8
7	0.25	1,375	1,708	30.5	47.0
	0.20	1,208	1,825	19.0	37.5
8	0.25	2,123	4,317	14.0	27.0
	0.20	3,150	6,933	8.5	19.1
9	0.25	4,883	10,133	15.5	28.3
	0.20	3,910	8,225	6.3	11.4
10	0.25	3,872	9,783	5.5	10.1
	0.20	1,013	1,487	11.8	20.8
11	0.25	3,038	3,642	11.2	19.8
	0.35	2,467	5,167	12.1	21.5
12	0.40	2,943	5,580	5.6	10.7

It is seen from the above data that leather tanned using the predominantly non-ionic, chromium-containing composition prepared in accordance with the method of the present invention by reacting lignin sulfonic acid with between 25-50% sodium bichromate by weight of the lignin solids, is markedly more resistant to abrasion and water absorption than leather tanned with a chromium-containing tanning composition prepared by reacting only 20% sodium bichromate by weight of the lignin solids. This clearly shows the superior properties of leather tanned in accordance with the present invention.

To further show the superiority of leather tanned in accordance with the present method, various commercially available vegetable tanned sole leathers are subjected to the abrasion and water absorption described hereinabove. The results of these tests are as follows:

Leather	Abrasion Cycles, 0.10 Inches	Percent Water Absorption	
		0.5 Hrs.	2.0 Hrs.
A	550	14.8	21.8
B	450	19.0	28.7
C	577	34.6	37.6
D	650	17.8	31.9
E	575		

From these results it is clearly seen that leather tanned in accordance with the present method has greatly superior resistance to abrasion than commercially available vegetable tanned sole leather.

Moreover, it will be appreciated that leather tanned in accordance with the present invention, i.e., in accordance with the method of Example 2, and retanned and fat liquored in accordance with the methods of Examples 3 and 5, respectively, exhibits good resistance to water absorption. However, as set forth hereinabove, increased resistance to water absorption can be obtained by subjecting the thus-tanned leather to further treatment, such as with a silicone resin, e.g., Dow Corning Silicone 1109. To show the effects of such further treatment, as well as to substantiate the fact that the superior abrasion resistance obtained by leathers tanned in accordance with the present invention is not due to the addition of a silicone resin, leathers produced in accordance with the method of Example 2 and then treated with varying amounts of the Dow Corning Silicone 1109, i.e., 0-15% by weight, are subjected to the abrasion and water absorption test described hereinabove. The results of these tests are as follows:

Test 1

Silicone, percent	Abrasion Cycles, 0.10 Inches	Percent Water Absorption	
		0.5 Hrs.	2.0 Hrs.
3	7,533	7.0	11.4
6	9,250	4.7	10.6
9	6,750	10.1	16.3
12	2,117	8.1	16.8
0	6,383	10.5	16.6

Test 2

Silicone, percent	Abrasion Cycles, 0.10 Inches	Percent Water Absorption	
		0.5 Hrs.	2.0 Hrs.
3	4,773	8.0	17.5
6	6,700	6.2	13.7
9	4,617	18.0	27.3
12	5,617	5.5	11.6
15	5,400	5.5	13.8
	6,300	9.3	16.8

From this data, it is clearly seen that the waterproofness of the leathers prepared in accordance with the present method is increased by treatment with a silicone resin and, additionally, that even where no silicone resin is added to the leather, the abrasion and water absorption resistance is still greater than that of leather tanned using a chromium-containing tanning material prepared by reacting lignin sulfonic acid with only 20% sodium bichromate by weight of the lignin solids.

EXAMPLE 7

To further demonstrate the advantage of leather tanned in accordance with the present invention, a series of actual field tests of leather is carried out by resoling one shoe of each of three pairs and observing the actual wear obtained in use. By this procedure, the following data are obtained.

Test Wearer	Experimental Sole	Control	Hours Worn	Comments
No. 1	1 Right	Left	360	Control worn—Replace both.
	2 Left	Right	610	Control worn—Replace control.
	3 Left	Right	224	Control worn—Experimental sound.
No. 2	1 Left	Right	263	Control worn—Replace control.
	2 Left	Right	945	Control worn—Experimental sound.

Control soles are good quality conventional vegetable tanned leather soles, all control soles being at least as thick as the experimental soles. All experimental soles were water-proofed with Dow Corning Silicone No. 1109.

In carrying out the above tests, it is found that the experimental soles give better traction on dry floors and pavement. Tests were concluded when the uppers are completely worn out, thus demonstrating that the sole should last the life of the shoe under fairly hard service.

EXAMPLE 8

Further to illustrate the practice of the present invention with respect to the effect of vegetable retanning and chrome retanning of leather produced in accordance with the present invention a series of chemical analyses and strength tests were carried out and indexed comparatively in the following table, the data reported being based on the weight of the tanned leather as is:

Sample	Percent H ₂ O	Percent Cr ₂ O ₃	Percent Ash	Grease	Percent Hide Substance	pH	Stitch Tear, #/In. ²	Tensile Strength, #/In. ²
A ¹	16.3	2.10	2.82	8.26	63.8	4.47	661	1,855
A plus Tanolin R Retan	17.5	4.18	4.82	5.15	61.6	3.57	887	2,138
A plus Vegetable Retan	15.9	1.69	2.23	6.04	54.9	3.97	885	2,910

¹ Tanned with composition produced by reaction of 25% sodium bichromate with 100% lignin solids.

The above data demonstrates that it is possible further to improve the strength of the strong, firm leathers obtained in accordance with the practice of this invention by proper retanning.

EXAMPLE 9

To demonstrate the analysis involved in determining the form of chrome in various reaction products of sodium bichromate and lignin sulfonic acid, a sample is prepared using sodium bichromate in the amount of 25% by weight, based on the lignin sulfonic acid content. An aliquot of this sample, in the form of an aqueous solution, is then passed through a cation exchange column filled with chloride-free Dowex 50-X1,¹ and a different aliquot is passed through an anion exchange column, filled with sodium-free Dowex 1-X1.² The effluent from each column is analyzed for chromium and the percentage of non-ionic, anionic and cationic chromium calculated. The results of such test is set forth in the following table:

Percent Sodium Bichromate	Percent Anionic Chromium	Percent Cationic Chromium	Percent Non-ionic Chromium
25	23.9	5.4	70.7

¹ Styrene type-sulphonic acid cation exchange resin.

² Styrene type-quaternary ammonium-chloride from anion exchange resin.

It is to be understood that although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited, since changes and alterations therein may be made which are within the full intended scope of this invention as defined by the appended claims.

What is claimed is:

1. In the tanning of leather the method which comprises the step of subjecting the material to be tanned to an aqueous solution of a predominantly non-ionic, chromium-containing reaction product obtained by chemically reacting lignin sulfonic acid with a hexavalent chromium compound in an amount within the range of 25% to about 50% by weight of the lignin sulfonic acid expressed as lignin solids, to obtain a reaction product containing a major proportion of non-ionic chromium.

2. In the tanning of leather according to claim 1 the further step which comprises retanning the thus-treated material with a vegetable tan.

3. In the tanning of leather in accordance with claim 1 the further step which comprises retanning the thus-treated material with a vegetable tan and fat liquoring the resultant leather.

4. In the tanning of leather in accordance with claim 1 the additional steps which comprise retanning the thus-treated material with a vegetable tan and subsequently fat liquoring and waterproofing the resultant leather.

5. In the tanning of leather in accordance with claim 1 the additional steps which comprise retanning the thus-treated material with a chrome tan and subsequently fat liquoring and waterproofing the resultant leather.

6. In the tanning of leather in accordance with claim 1 the further step which comprises retanning the thus-treated material with a chrome tan.

7. In the tanning of leather in accordance with claim

6 the further step which comprises fat liquoring the thus-treated material.

8. The process of tanning leather which comprises subjecting a pickled hide to a liquid composition comprising the reaction product obtained by chemically reacting a solution of lignin sulfonic acid prepared by mineral acid acidification of an aqueous solution of water-soluble lignin solids with a solution of at least 25% and not more than about 50% by weight of sodium bichromate based on the lignin solids content, at an elevated temperature until the desired tanning is effected and thereafter adding alkali partially to neutralize the stock to a higher acid pH and thereafter washing the thus-tanned leather.

9. The method of tanning which comprises floating a pickled hide in an alkali metal chloride solution and adding thereto a liquid tanning composition comprising the reaction product of lignin sulfonic acid and a hexavalent chromium compound in an amount within the range of 25% to about 50% by weight of the lignin sulfonic acid expressed as lignin solids to produce a predominantly non-ionic, chromium-containing, tanning composition, for about 2 hours at a temperature of about 100° F., thereafter adding an alkali metal bicarbonate solution to raise the pH of the solution to a higher acid pH and continuing the tanning until a shrink temperature of about 200° F. is obtained, and thereafter washing the thus-treated leather.

10. A process according to claim 9 wherein the thus-treated leather is retanned.

11. The method of tanning which comprises floating a pickled hide in an alkali metal chloride solution and adding thereto a liquid tanning composition comprising the reaction product of lignin sulfonic acid and a hexavalent chromium compound in an amount within the range of 25% to about 50% by weight of the lignin sulfonic acid expressed as lignin solids to produce a predominantly non-ionic, chromium-containing, tanning composition, for about 8 hours at a temperature of about 90° to 120° F., thereafter adding an alkali metal bicarbonate solution partially to raise the pH of the solution to a higher acid pH and continuing the tanning until a shrink temperature of about 200° F. is obtained, and thereafter washing the thus-treated leather.

12. The method of tanning which comprises subjecting a hide to an aqueous solution of the reaction product obtained by chemically reacting a major proportion of lignin sulfonic acid as prepared by dissolving the lignin solids in water and acidifying the resultant solution, with a lesser proportion of a hexavalent chromium compound, the amount of hexavalent chromium compound being within the range of 25% to 50% by weight of the lignin solids to produce a predominantly non-ionic, chromium-containing reaction product, for a time sufficient to obtain a high leather shrink temperature and thereafter neutralizing and washing the thus-prepared leather.

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