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METHOD OF RETANNING OF CHROME LEATHER

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The two principal current methods of converting raw pelt into leather are: (*a*) vegetable tannage (*b*) chrome tannage. Vegetable tannage imparts more weight to the skin, but the leather is not resistant to hot water. Chrome tannage confers resistance to hot water, and in addition the process is more rapid than with vegetable tannage. Chrome tannage by itself however gives an empty-feeling leather, and a supplementary subsequent tannage with vegetable tanning materials is usually given. The degree of this subsequent tannage may vary from a mild retannage with from—

2 to 5 percent of a vegetable tanning material for the purpose of mordanting, up to a thorough retannage with as high as 50% of vegetable tanning material. These percentages are based on the weight of the skins.

In applying the supplementary tannage it is common practice to neutralize the leather prior to the application of the vegetable tannage. This neutralization is ordinarily carried out in a direct manner by bringing the leather in intimate contact with suitable amounts of alkali by drumming or paddling in solutions of an alkali. The neutralizing may also be carried out indirectly, as for instance when the subsequent tannage is carried out in vats where the proportion of vegetable tanning liquor is high in relation to the amount of leather being retanned. In such a case the vegetable tan liquor, containing as it does a considerable proportion of the salts of weak acids, buffers the relatively strong acids present in the chrome tanned leather. In whatsoever manner the neutralization is effected it is essential to give the supplementary tannage at a high pH, in order to avoid producing a harsh, tender or unevenly retanned leather. In practice, therefore, the leather is neutralized as much as is safe, the limit being determined by the appearance of a rough or "drawn" grain. Too much neutralization gives a rough grained, spongy leather. Thus the safe working range for a successful retannage with vegetable materials is narrow, and care must always be exercised or the leather will suffer from retannage in too acid a condition, or from over-neutralization.

Chrome leather may be given a supplementary tannage with synthetic tanning agents from the class consisting of condensed aromatic sulfonic acids, aromatic sulfonic acids of high molecular weight, and resins peptized in aromatic sulfonic acids. The surprising feature of my invention is the discovery that this supplementary tannage may be carried out without a prior neutralization of the leather. This feature is an important step forward in the art, as it enables the production of a retanned or mordanted chrome leather without any danger of affecting the leather adversely by the neutralization process.

The chrome leather may be taken as it comes from the tanning drums or paddles, and after washing with water to remove the free excess chrome salts is given a supplementary tannage with these synthetic tanning agents. The resulting leather has a smoother grain and a stronger fibre than a leather retanned with a vegetable tanning material. For the purpose of obtaining the smoothest grain and strongest fibre it is preferable to take the leather in a quite acid condition. Inasmuch as some chrome leathers come from the tanning operation less acid than others it is advisable in some cases to add acid prior to this supplementary tannage. This advisability may be simply determined by dropping a few drops of suitable indicator on a cut surface of the leather and noting the apparent pH value by the color assumed by the indicator. I prefer to carry out the supplementary tannage on leather which shows an apparent pH of less than 5. In cases where the most acid conditions are desired, the supplementary tannage may be given immediately subsequent to the chrome tannage in the spent tanning liquor without removing the leather from the tanning drum. The supplementary tannage may vary in amount from: 2% to 50% of the synthetic tanning materials, based on the weight of the skins and is carried out in the regular manner in regular apparatus. The leather is washed after the retannage and then colored, fatliquored and finished as usual.

The following examples serve to illustrate how I carry out my invention, but my invention is not limited to these examples. It is further expressly understood that the synthetic tanning material is one of the class consisting of:

(*a*) Condensed aromatic sulfonic acids, such as phenol sulfonic acid condensed with formaldehyde, acetaldehyde, benzaldehyde, acetone, cyclohexanone; naphthalene sulfonic acid condensed with these aldehydes or ketones; materials similar to the above but derived from homologues of phenol or naphthalene.

(*b*) Aromatic sulfonic acids of high molecular weight, such as phenanthrene monosulfonic acid; substituted naphthalene sulfonic acids like benzyl- or dibenzyl-naphthalene sulfonic acids; carbazole sulfonic acid; tetralin sulfonic acid.

(*c*) Aromatic sulfonic acids containing dispersed resins such as benzyl-naphthalene sulfonic

acid or tetralin sulfonic acid containing peptized phenol-formaldehyde resin.

Example 1

400 lbs. of calfskins, tanned by any customary one-bath chrome process are taken from the tannage, shaved and then washed in a drum for 10 minutes with water at 70° to 80° F. A cut made in the neck of the wet leather should at this stage show a yellow to green coloration when wet with a 1/10% solution of brom cresol green, indicating an apparent pH value of the stock between 4 and 4½ units. The skins are then drummed with 50 gallons of water and 40 lbs. of a synthetic tanning material prepared as follows:

3.7 lbs. of phenol

4.2 lbs. of sulphuric acid (66° Beaumé) are mixed and heated at 100° for 2 hours. The water soluble mixture is cooled to 30° C. and diluted with 1.1 lbs. water. 1.7 lbs. of formaldehyde (37%) is added slowly with good stirring and cooling, and the stirring continued for 5 hours thereafter at a temperature of 25–30° C. The mixture is diluted somewhat and

1.1 lbs. of caustic soda added in rather strong solution while cooling. The resulting solution is diluted to 40 lbs.

The drumming is continued for 30 minutes, whereupon the skins are washed for a further 30 minutes, with a good stream of water passing through the drum. The skins may then be colored with direct or acid dyes, topped if desired with basic dyes, or dyed entirely with basic dyes, fatliquored and finished in the regular manner.

Example 2

400 lbs. of kidskins tanned by a regular two-bath chrome process are taken from the hypo reduction bath and washed to free them from excess hypo, then shaved and washed 10 minutes in order to wash them free of adhering shavings. A cut is made in the neck of several skins and the apparent pH value estimated by dropping a 1/10% solution of brom cresol green on the cuts. If this indicator indicates a pH value of over 4.5 units, but not otherwise, I add 4 lbs. muriatic acid 20° previously diluted in a bucket of water to the leather in the drum with 50 gallons of water, and drum for 15 minutes. I then add 25 lbs. of a synthetic tanning agent prepared as below, and drum a further 20 minutes.

2.85 lbs. of 4-4'-dihydroxydiphenyldimethyl methane (Beilstein Band VI p. 1011) are sulphonated by heating with 2.5 lbs. of conc. sulphuric acid at 70° C. for 5 hours. The excess of sulphuric acid is neutralized with caustic soda and the solution diluted to 25 lbs.

The leather is then washed in the same drum for 30 minutes with a good stream of water passing through the drum, and the coloring, fatliquoring and drying of the leather follow in the regular manner.

Example 3

To 800 lbs. of chrome side leather tanned by the regular one-bath process and showing an apparent pH value between 4.5 and 5.5 units I add sufficient sulphuric acid to reduce the apparent pH value to between 3 and 3.25 units. This operation is done by drumming the leather for 30 minutes in 150 gallons water and adding the acid, previously diluted in a bucket of water, while the drum is running. The amount of acid required depends on the apparent pH value of the stock, but between 2 lbs. and 4 lbs. should be sufficient. The leather lies in this acid liquor overnight, or about 16 hours and is again drummed 10 minutes. Thereupon 50 lbs. of a synthetic tanning material prepared as described below is added while the drum is running, and the drum run a further period of 30 minutes. 12.8 lbs. naphthalene are sulphonated by heating with 15.0 lbs. sulphuric acid 98% until all is completely soluble in water. The solution is cooled, diluted with water, and 16.2 lbs. formaldehyde 37% aqueous solution added. The mixture is heated at 90° C. until condensation is complete, then diluted with water, 4 lbs. caustic soda added to neutralize the excess of mineral acid, and the final weight adjusted by addition of water to give 130 lbs. After treatment with this solution the leather is washed, and when the apparent pH value has risen to between 4.5 and 5.0 units it is given a thorough retannage with liquid quebracho extract. This operation may be carried out in the same drum or in a paddle, or by hanging the sides in a vat of quebracho liquor.

Example 4

800 lbs. of chrome side leather tanned by a regular one-bath chrome process and retanned with a further amount of chrome in the regular manner are washed 10 minutes and a few drops of a 1/10% solution of brom cresol green dropped into a cut. If this indicator indicates by a blue color an apparent pH value of over 4.5 units I add to the leather and water in the drum sufficient sulphuric acid, previously diluted in a bucket of water, to reduce the apparent pH value of the stock to 3.5 units. The leather is drummed with this acid solution for 1 hour, whereupon I add 80 lbs. of a synthetic tanning material prepared as follows:

A mixture of

9 lbs. of naphthalene

9 lbs. of sulphuric acid 98% is heated to 130° C. for 6 hours, then cooled to 100° C. Then

21 lbs. of dibenzylnaphthalene

9.7 lbs. of sulphuric acid 70% are added.

Temperature is adjusted to 85° and

7.2 lbs. of formaldehyde 37% are run in over a period of 2 hours, while the mixture is well stirred. Stirring is continued at 85–90° C. for 4 hours. The mixture is then diluted with 90 c.c. water and the excess of mineral acid neutralized with caustic soda, given in concentrated solution. The product is diluted to 80 lbs. In this way a creamy liquid is produced which disperses readily in water.

Drumming is continued for a further period of 1 hour. The leather is then washed for 1 hour with a good stream of water passing through the drum, when it is ready for coloring, fatliquoring and finished in the regular manner.

Example 5

600 lbs. of pickled sheepskins are put in a drum with 42 gallons of a 5% salt brine and drummed 5 minutes. While the drum is still running, 11 lbs. of chromic oxide in the form of a basic chromium sulfate of 65% acidity are added in two feeds, one hour apart. One hour after the second feeding, while the apparent pH value of the skins is below 3 units, 42 lbs. of a synthetic tanning material prepared as described below are added and the drum run a further 30 minutes.

12 lbs. tetrahydronaphthalene are added to 16.3 lbs. sulphuric acid 98% at 100° C. The mixture is stirred at this temperature until all is

completely soluble in water, then diluted with water and completely neutralized with lime to remove excess of mineral acid. The filtered solution is reacidified with 8 lbs. sulphuric acid, allowed to settle several days, and the clear liquor drawn off. The weight is adjusted by addition of water to give 100 lbs. Sufficient bicarbonate of soda is now added to raise the apparent pH value of the leather to 3¾ units. With the drum standing still, water is now added until the leather is well covered; the drum run 10 minutes to mix the contents thoroughly. The following morning the leather is well washed with a good stream of water in the same drum and removed for coloring, fatliquoring and drying by the usual methods.

It is to be understood, of course, that the above examples are merely illustrative of the processes intended to be covered by this application and I am in no way confined to the methods of operation, temperatures, proportions of ingredients, etc., except as indicated in the claims which follow, since it is obvious to anyone versed in the art that wide deviations are possible without departing from the scope of this invention. In the above examples methods are given for preparing the tanning materials but it is to be understood that the following claims cover the materials listed at page 1, line 97 to page 2, line 2 of the patent, no matter how prepared since the method of preparation is immaterial.

It is understood that in the following claims the words "apparent pH value" mean the pH value as estimated by the use of 1/20% solutions of the following indicators thymol blue, bromphenol blue, brom-cresol green, brom cresol purple, when employed according to the methods described in the above examples.

What I claim is:

1. In the making of leather the step of retanning chrome leather which comprises the application of synthetic tanning materials belonging to the class consisting of condensed aromatic sulfonic acids, aromatic sulfonic acids of high molecular weight, and resins peptized in aromatic sulfonic acids, without neutralizing the leather prior to retannage.

2. In the making of leather the step as described in claim 1 in which the retanning is carried out at an apparent pH value of between 2½ and 5 units.

3. In the making of leather the step of retanning chrome leather after fixation of the chrome tannage, which comprises the application of aromatic sulfonic acids at an apparent pH value of between 2½ and 5 units.

4. In the making of leather the step as described in claim 3 in which the synthetic tanning materials are aromatic sulfonic acids of high molecular weight.

5. In the making of leather the step as described in claim 3 in which the synthetic tanning materials are resins peptized in aromatic sulfonic acids.

6. In the making of leather the step of retanning chrome leather after fixation of the chrome tannage, which comprises the application at an apparent pH of 2½ to 5 units of phenol sulfonic acid condensed with an aldehyde.

7. In the making of leather the step of retanning chrome leather, after fixation of the chrome tannage, which comprises the application at an apparent pH of 2½ to 5 units of phenol sulfonic acid condensed with formaldehyde.

8. In the making of leather the step of retanning chrome leather, after fixation of the chrome tannage, which comprises the application at an apparent pH of 2½ to 5 units of a sulfonic acid of a phenol condensed with formaldehyde.

9. In the making of leather the step of retanning chrome leather, after fixation of the chrome tannage, which comprises the application at an apparent pH of 2½ to 5 units of naphthalene sulfonic acid condensed with an aldehyde.

10. In the making of leather the step of retanning chrome leather, after fixation of the chrome tannage, which comprises the application at an apparent pH of 2½ to 5 units of naphthalene sulfonic acid condensed with formaldehyde.

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