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TANNING PROCESS

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5 Claims

ABSTRACT OF THE DISCLOSURE

Tanning process in which the material to be tanned is drummed with an aqueous solution containing a methylol derivative of a mononuclear or binuclear phenol containing in its nucleus not more than one phenolic hydroxyl group and being free from anionic groups and from condensed rings. The process produces soft, nonbrittle leathers and fur skins having a substantial resistance to alkalies, a high shrinking temperature, and good light fastness.

This invention relates to a new tanning process in which methylol derivatives of mononuclear or binuclear phenols are used as tans. It also relates to leathers and furs prepared by the said process.

The production of synthetic tans by condensation of phenolic compounds containing sulfonic acid groups with formaldehyde or of phenols with formaldehyde followed by the introduction of sulfonic acid groups has been known for a long time. The need for the introduction of acid groups into the condensation products arises from the poor water-solubility of such products. It is known that the optimum effectiveness of these tans lies in the strongly acid pH range at about 3.5. Above this pH range, the tanning action is inadequate. As a general rule it may be said that the sulfonic acid groups counteract the tanning. It has therefore been proposed to carry out tanning with aromatic hydroxy compounds not having sulfonic acid groups. Thus it is known that the skin may be treated with water-soluble or water-emulsifiable phenols, such as resorcinol or naphthol, followed by treatment with formaldehyde, or vice versa. Simultaneous treatment of the skin with formaldehyde solution and naphthols is also known. These methods have the disadvantage that they very readily give hard, brittle leather whose quality is not satisfactory.

It is an object of this invention to provide a process for preparing soft, nonbrittle leathers and fur skins in a particularly simple way. Another object of this invention is to provide a process for preparing leathers and fur skins having great resistance to alkalies, a high shrinking temperature and good light fastness.

These and other objects are achieved by using methylol derivatives of mononuclear or binuclear phenols containing a maximum of one phenolic hydroxyl group in each nucleus and being free from anionic groups and from condensed rings as tans in the weakly acid to weakly alkaline range. It is preferred to use phenols which, besides the phenol nuclei, contain not more than four aliphatic carbon atoms or not more than one phenyl radical or benzyl radical to each phenolic hydroxyl group.

Examples of methylol derivatives of the abovementioned type are monomethylol and polymethylol compounds of phenol itself, low molecular weight alkylphenols, for example the cresols, xlenols, thymol and carvacrol, halophenols, phenylphenols, monohydroxydiphenylmethanes and bis-phenols, for example dihydroxydiphenylmethanes, dihydroxydiphenylpropanes, and dihydroxydiphenylsulfones. The methylol compounds of 4,4'-

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dihydroxydiphenylsulfone have proved to be particularly suitable.

Methylol compounds of phenols are known. It has been thought hitherto however that they were unsuitable as tans. In fact in the strongly acid pH range conventionally used for tanning they have no tanning action. According to the present invention they are therefore preferably used near to the neutral point; the effective pH range extends from about 6 to about 9. If methylol compounds of phenols are used for tanning pelts, it is particularly simple to carry out the tanning at the pH value which the delimed or drenched pelts have without any additional measures.

Apart from this, it has proved to be particularly suitable to adopt the following procedure for tanning:

The material to be tanned, e.g. delimed and drenched pelts or leather to be retanned, has added to it 1 to 30%, for pretannage preferably 1 to 10%, for self-tannage preferably more than 10% on the weight of the material to be tanned of the methylol compound dissolved in water at room or slightly elevated temperature or if desired in mixtures which contain not only water but also up to 50%, preferably up to 20% (on the total weight of the mixture) of water-soluble organic solvents, in particular low molecular weight alcohols and ketones, for example methanol, ethanol and acetone, and then milled until it has been tanned uniformly and thoroughly in section. The time required for this is one to ten hours, depending on the thickness of the material to be tanned. The tanned material may then be further treated in the conventional way, but it may also be merely dried and kept for subsequent finishing.

Particularly good results are obtained by acidifying the material thus tanned in the liquor, preferably to a pH value of 4 to 4.5, whereby the fullness of the leather is improved and only then proceeding with the further treatment. Acids conventionally used in tanning, e.g. sulfuric acid, hydrochloric acid, acetic acid, oxalic acid and preferably formic acid, may be employed for acidification.

The methylol compounds may be used as self-tannins. They constitute white tannins having good light fastness. Leather prepared in this way may be dyed, buffed and finished well. The methylol compounds are also very suitable as pretannins because pretanned leather obtained therewith may be retanned well for example with chrome tannins, aluminum tannins, synthetic and vegetable tannins. In vegetable retannage, for example with quebracho, mimosa or chestnut, very pale, cream-colored leather is obtained. The methylol compounds are also suitable as pretannins for rapid vegetable tanning of heavy types of leather because they greatly accelerate the penetration of the vegetable tannins.

The said tannins may also be used with good results for retannage.

The new tans are very suitable for tanning fur skins, the high shrinkage temperatures being of particular importance for the subsequent dyeing in a hot liquor.

The invention is illustrated by the following examples in which the percentages are on the weight of the material to be tanned.

EXAMPLE 1

Delimed and bated calf pelts are drummed with 100% of water (temperature 25° C.) and 10% of monomethylol-4,4'-dihydroxydiphenyl-sulfone until they are thoroughly tanned (about six hours). The leather obtained may be dried and kept for subsequent retannage.

EXAMPLE 2

The leather prepared according to Example 1 is wetted back, acidified to about pH 4.5 with formic acid and retanned in the conventional way with:

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- (a) 10% of a mixture of vegetable tannins (one-third quebracho, one-third mimosa and one-third chestnut),
 (b) 6% of basic chromium sulfate,
 (c) 10% of commercial synthetic tannin which has been prepared by condensation of phenolsulfonic acid with urea and formaldehyde followed by condensation of the intermediate product obtained with phenol and formaldehyde.

All the leathers obtained exhibit fine smooth grain. The leather obtained according to 2(b) is capable of withstanding the boiling test. Leather obtained according to 2(c) is white and fast to light.

EXAMPLE 3

Calf pelts are tanned as described in Example 1 and then acidified with formic acid to about pH 4.5 in the tanning liquid itself. Retannage is carried out as in Example 2(a) to 2(c). The leather obtained has better fullness than that according to Example 2.

EXAMPLE 4

Delimed and bated split cowhides are milled with 200% of water (temperature 30° C.) and 30% dimethylolphenol at pH 9 until thoroughly tanned (about eight hours), and then rinsed, stuffed and dried. The leather is soft and has a slight yellowish red coloration.

EXAMPLE 5

The procedure of Example 4 is followed but after tanning the material is acidified in the tanning liquor to pH 4.5 with formic acid and the further procedure of Example 4 is followed. The leather obtained has better fullness than that of Example 4.

EXAMPLE 6

Unsplit delimed and bated cowhides are milled with 200% of water (temperature 30° C.) and 3% of monomethylolphenol at pH 8 for four hours, then acidified in the tanning liquor with formic acid to pH value 4.0 to 4.5. The liquor is drained off and the leather is drummed with 30% of water, 10% of quebracho (P.T.), 10% of mimosa (P.T.) and 10% of chestnut (P.T.) until the material is uniformly and thoroughly tanned. The leather obtained, without further bleaching, is pale in color, full and gives a good yield value.

EXAMPLE 7

Delimed and bated sheep's pelts are milled with 50% of water (temperature 30° C.) and 20% dimethylol-4,4'-dihydroxydiphenylsulfone at pH 8.5 for four hours and then the tanning liquor is acidified with formic acid to pH 4.0 to 4.5. After the leather has been milled for about another two hours, it is rinsed, fat-liquored and dried. A white full leather having a shrinkage grain is obtained.

EXAMPLE 8

Dry chrome calf is wetted back with 100% of water at 35° C. and 2% of formic acid for three hours. The leather is then milled with 90% of water and 20% of dimethylol-4,4'-dihydroxydiphenylsulfone at pH 9 for five hours. 5%

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of formic acid is then added to the tanning liquor, and milling is continued for another hour. The tanned material is lightly set out, dry-drummed for 15 minutes, dried, sawdusted and milled. A shrunken grain leather is obtained.

We claim:

1. A tanning process which comprises: drumming the material to be tanned until the material is uniformly tanned throughout its thickness with a solution consisting essentially of water or water and up to 50% by weight calculated on the liquid of a water-soluble organic solvent selected from the group consisting of a low molecular weight alcohol and a low molecular weight ketone and as an essential tanning agent a methylol compound, said methylol compound being a monomethylol or dimethylol derivative of a compound selected from the group consisting of phenol, cresol, xyleneol, thymol, carvacrol, phenylphenol, monohydroxydiphenylmethane, dihydroxydiphenylmethane, dihydroxydiphenylpropane and 4,4'-dihydroxydiphenylsulfone, such methylol compound being applied in an amount of 1 to 30% by weight calculated on the material to be tanned and said solution having a pH-value of from 6 to 9.

2. A process as claimed in claim 1 wherein the tanning solution contains as essential tanning agent a methylol compound selected from the group consisting of monomethylol and dimethyl derivatives of 4,4'-dihydroxydiphenylsulfone.

3. A process as claimed in claim 1 wherein the tanning solution contains as essential tanning agent a methylol compound selected from the group consisting of a monomethylol and dimethylol derivative of phenol.

4. A process as claimed in claim 1 wherein the tanned material is acidified in the tanning liquor to a pH value of 4 to 4.5 prior to further processing.

5. Leathers or fur skins which have been tanned in accordance with the process as claimed in claim 1.

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