

1

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TANNING WITH A HEMIACETAL AND RESORCINOL OR PYROGALLOL SOLUTION

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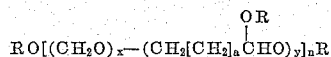
(Granted under Title 35, U.S. Code (1952), sec. 266)

A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This invention relates to the tanning of skins. More particularly, this invention relates to an in situ polymeric tannage employing "Aldocryl" and a phenol.

By skins are meant all animal skins, such as cowhide, horsehide, calfskin, goatskin, sheepskin, pigskin, and fur skins, which are tanned commercially.

"Aldocryl" is the trade name for a hydroxy-containing hemi-acetal obtained as a condensation product of acrolein and formaldehyde. It is not a single chemical, but is a mixture of compounds represented by the formula



wherein at least one R is hydrogen and the remaining R's are members of the group consisting of hydrogen and alkyl radicals, x is an integer of 1 to 5, a is an integer of 1 to 8, y is an integer of 1 to 5, and n is an integer of at least 2.

Hemi-acetals are not expected to be effective tanning agents, but "Aldocryl" tannage produces a firm, flat white leather. In addition to lack of fullness the product has a low shrink temperature (T_s 81–83° C.). This shrink temperature is typical of an organic tannage, being comparable to that of a vegetable (natural organic) tanned leather or of the best synthetic tannin, such as a sulfonated phenol-formaldehyde polymer.

Many phenols, such as resorcinol, have no tanning ability per se. When employed as the sole agent in a tanning system they are only weakly bonded to the skin and are readily removed by washing the skin. Combination tannages with phenols, such as phenols and aldehydes, are not generally applicable. Moreover, phenol-aldehyde tannages give products which are unstable to light and will darken with aging even in the absence of light.

We have discovered, however, that the combination tannage of "Aldocryl" and a phenol such as resorcinol or pyrogallol gives a leather product from a domestic sheepskin which is full, mellow, does not darken in light, has an exceptionally high shrink temperature, and is resistant to shrinkage by perspiration.

According to the present invention skins are tanned by a process comprising impregnating the skins with a buffered aqueous solution at pH in the range of about 4.0 to 5.0 containing "Aldocryl" and a phenol selected from resorcinol and pyrogallol and adjusting the pH of the solution during the tanning process to a pH of about 7.5–8.5.

The tannage gives an inherently mellow leather. This is presumably because the tanning molecules formed in situ are relatively low in molecular weight. The reaction between the "Aldocryl" and resorcinol is interrupted and terminated by reaction with the protein.

For any given amount of tanning material, the present tannage appears to be more effective than a vegetable tannage in producing a "full" leather.

2

The leather has high thermal stability. Domestic sheepskin can be tanned to give a leather which does not shrink in boiling water in 5 minutes. This degree of tannage is not necessary, but is cited to illustrate the potential of the new combination tannage. The high heat resistance obtainable in "Aldocryl-resorcinol" tanned leather allows the tanned skin to be fat-liquored and finished in normal production manner, whereas vegetable tanned skins require special handling.

Tannages were performed with various ratios of "Aldocryl" and phenol, and over a range of total amounts of tanning agent added, and the results compared with aldocryl tannages conducted for control purposes.

A typical procedure is as follows:

A pickled sheepskin (usually a 100 gm. sample) was placed in a container with 100% water float, 10% by weight of a 10% solution of sodium sulfate, and 3% sodium acetate, all based on pickled weight of the skin, and turned for one-half hour at 90° F. to depickle the skin. At this time the pH of the solution is about 4.7. The tanning agent was added and turning continued one hour. The pH of the solution, typically about 4.5, was adjusted to pH 7.8–8.0 by adding sodium bicarbonate in 3 feeds. The churn was turned for two hours more with the system at 90–95° F.

After a total of 4 hours in the tanning solution, the skin was removed, a sample taken for shrink temperature measurements, the skin was washed for one-half hour in running water, horsed to drain, and acidified with 1% sulfuric acid to about pH 4.0–4.5 in preparation for fat-liquoring and finishing.

In Table 1 are summarized data obtained following the typical procedure and varying the tanning agents.

Some of the sets of data are selected from two or more tannages conducted under similar conditions to give leather with an identical shrink temperature. Duplicates have been omitted from the table for purposes of clarity in analyzing the data.

TABLE I.—TANNAGE OF DOMESTIC SHEEPSKIN

Example No.	Tannage ¹			Ratio A-R ²	T _s ³ °C.
	"Aldocryl", percent	Resorcinol, percent	Total, percent		
1	5	—	5	—	82
2	10	—	10	—	83
3	20	—	20	—	82
4	2	2.5	4.5	1-1	80-82
5	6	7.5	13.5	1-1	85-86
6	6.4	8.0	14.4	1-1	88
7	8	10.0	18.0	1-1	88
8	12	10	22.0	1.5-1	89
9	3.04	1.9	4.94	2-1	83
10	6.24	3.8	10.04	2-1	87
11	12.0	7.5	19.5	2-1	97
12	5.0	2.5	7.5	2.5-1	94
13	10.0	5.0	15.0	2.5-1	92
14	3.6	1.5	5.1	3-1	92
15	6.0	2.5	8.5	3-1	94-96
16	7.2	3.0	10.2	3-1	97
17	12.0	5.0	17.0	3-1	100
18	12.0	2.5	17.5	6-1	92-94

¹ Based on wet weight of sheepskin.

² Ratio of moles "Aldocryl" to moles resorcinol.

³ Shrink temperature at completion of tanning. T_s is usually increased several degrees after acidification.

⁴ 5 minutes boil.

The spent tanning solutions were tested for presence of phenols. The tests were usually negative, confirming the participation of the resorcinol in the tannage.

Tannages were also conducted with combinations of "Aldocryl" and pyrogallol and "Aldocryl" and catechol, as described in Examples 19 and 20.

Example 19

The depickling and tannage followed the typical procedure and varied from Example 15 in that the tanning agents added to a 100 gm. sample of sheepskin were 5.12 gms. "Aldocryl" and 2.5 gms. pyrogallol, a total of 7.62%, and a 3 to 1 molar ratio of "Aldocryl" to phenol. The shrink temperature is 88-91° C. In general, the leather had an appearance similar to that of Examples 14 and 15.

Example 20

This process was identical with Example 15, except that catechol was substituted for resorcinol. The shrink temperature is 83° C. This is the shrink temperature of an "Aldocryl" tannage. There is no evidence of a combination tannage.

Although the shrink temperature of leather is not per se indicative of the overall properties of a leather, it is generally accepted as an important criteria of degree tannage.

The examples show that for all "Aldocryl-resorcinol" tannages, from a 1-1 molar ratio to at least a 3-1 molar ratio combination, the shrink temperature tends to increase with increase in amount of tanning agent employed. This is in contrast to tannage with "Aldocryl" alone, where, as illustrated in Examples 1-3, there is no improvement in shrink temperature. The optimum combination is indicated to be in the range of about 2.5-1 to 3-1. This tannage achieves a significant increase in shrink temperature with a small amount of tanning agent. With a 3-1 molar ratio of "Aldocryl" to resorcinol a shrink temperature of over 90° C. was obtained with a total of 5% tanning agent. The effectiveness of this tannage makes it possible to vary the process to obtain the desired amount of fullness and mellowness and to have high thermal stability in all the leather products.

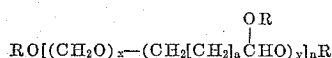
Although resorcinol is the preferred phenol, pyrogallol may also be used in the new in situ tannage. Catechol appears to be unreactive.

The "Aldocryl-resorcinol" tannage is particularly effective in providing perspiration resistance to the leather product, as determined by the standard test in which the leather sample was soaked for 2 hours in a standard, synthetic perspiration solution and then heated in a humid atmosphere at 70° C. for 48 hours. Leather products, both from domestic sheepskin and from cabretta skins, tanned with resorcinol and "Aldocryl" remained flat and flexible and changed very little in shape and area. Tests performed on leather which had been stored for six months or longer indicate that this property may be retained indefinitely.

An unusual characteristic of the leather products of this tannage is the reaction to light. Instead of darkening, as is typical of a tannage in which a phenol is employed, the exposed samples did not become darker, but remained unchanged or became slightly lighter in color.

We claim:

1. A tanning process comprising impregnating skins with a buffered aqueous solution at a pH in the range of about 4.0 to 5.0 containing a hemi-acetal of the formula

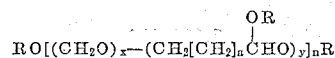


wherein at least one R is hydrogen and the remaining R's are members of the group consisting of hydrogen and alkyl radicals, x is an integer of 1 to 5, a is an integer of 1 to 8, y is an integer of 1 to 5, and n is an integer of at least 2 and a phenol selected from the group consisting of resorcinol and pyrogallol and adjusting the pH of the solution during the tanning process to a pH in the range of about 7.5 to 8.5.

2. The process of claim 1 in which the phenol is resorcinol.

3. The process of claim 1 in which the phenol is pyrogallol.

4. A tanning process comprising impregnating skins with a buffered aqueous solution at a pH in the range of about 4.0 to 5.0 containing a hemi-acetal of the formula

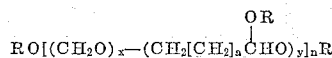


wherein at least one R is hydrogen and the remaining R's are members of the group consisting of hydrogen and alkyl radicals, x is an integer of 1 to 5, a is an integer of 1 to 8, y is an integer of 1 to 5, and n is an integer of at least 2 and a phenol selected from the group consisting of resorcinol and pyrogallol, said hemi-acetal and said phenol being present in a molar ratio of about from 1-1 to 3-1 hemi-acetal to phenol, and adjusting the pH of the solution during the tanning process to a pH in the range of about 7.5 to 8.5.

5. The process of claim 4 in which the phenol is resorcinol.

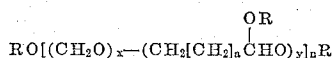
6. The process of claim 4 in which the phenol is pyrogallol.

7. A tanning process comprising impregnating skins with a buffered aqueous solution at a pH in the range of about 4.0 to 5.0 containing in the range of about 13.5 to 18%, based on weight of the skin, of a 1 to 1 molar ratio of a hemi-acetal of the formula



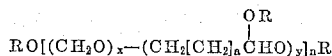
wherein at least one R is hydrogen and the remaining R's are members of the group consisting of hydrogen and alkyl radicals, x is an integer of 1 to 5, a is an integer of 1 to 8, y is an integer of 1 to 5, and n is an integer of at least 2 and resorcinol and adjusting the pH of the solution during the tanning process to a pH in the range of 7.5 to 8.5.

8. A tanning process comprising impregnating skins with a buffered aqueous solution at a pH in the range of about 4.0 to 5.0 containing at least about 5%, based on weight of the skin, of a 2 to 1 molar ratio of a hemi-acetal of the formula



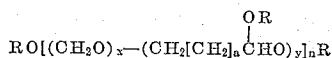
wherein at least one R is hydrogen and the remaining R's are members of the group consisting of hydrogen and alkyl radicals, x is an integer of 1 to 5, a is an integer of 1 to 8, y is an integer of 1 to 5, and n is an integer of at least 2 and resorcinol and adjusting the pH of the solution during the tanning process to a pH in the range of 7.5 to 8.5.

9. A tanning process comprising impregnating skins with a buffered aqueous solution at a pH in the range of about 4.0 to 5.0 containing about from 5 to 17%, based on weight of skin, of a 3 to 1 molar ratio of a hemi-acetal of the formula



wherein at least one R is hydrogen and the remaining R's are members of the group consisting of hydrogen and alkyl radicals, x is an integer of 1 to 5, a is an integer of 1 to 8, y is an integer of 1 to 5, and n is an integer of at least 2 and resorcinol and adjusting the pH of the solution during the tanning process to a pH in the range of 7.5 to 8.5.

10. A tanning process comprising impregnating skins with a buffered aqueous solution at a pH in the range of about 4.0 to 5.0 containing about 5%, based on weight of skin, of a 3 to 1 molar ratio of a hemi-acetal of the formula



wherein at least one R is hydrogen and the remaining R's are members of the group consisting of hydrogen and alkyl radicals, x is an integer of 1 to 5, a is an integer of 1 to 8, y is an integer of 1 to 5, and n is an integer of at least 2 and a phenol selected from the group consisting of resor-

5

cinol and pyrogallol, and adjusting the pH of the solution during the tanning process to a pH in the range of 7.5 to 8.5.

11. The process of claim 10 in which the phenol is resorcinol.

12. The process of claim 10 in which the phenol is pyrogallol.

5

6

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NORMAN G. TORCHIN, *Primary Examiner.*