THE TANNING ACTION OF A HEMIACETAL IN COMBINATION WITH RESORCINOL

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ABSTRACT

An *in situ* tannage using resorcinol with a condensation product of acrolein and formaldehyde is described. Some reaction takes place in the skin at a pH of 4.7 and tanning is completed at a pH of about 8.0. A Mannich-type mechanism is postulated.

Experimental tannages carried out on domestic sheepskins and New Zealand lambskins were finished into work glove and suede garment leathers, respectively.

The physical properties of the leathers compared favorably with conventionally processed sheepskins. The leathers also exhibited marked resistance to deterioration from perspiration.

INTRODUCTION

This paper will describe the tanning action of an acrolein-formaldehyde condensation product in combination with resorcinol. The tanning molecules are formed in the presence of the skins in an *in situ* tannage.

Formaldehyde is a well-known tanning agent, and acrolein has been evaluated previously (1). Resorcinol has no tanning action by itself, but it has been used in conjunction with other compounds. Windus developed an *in situ* tannage using formaldehyde and resorcinol (2). The procedure was later extended to include tetrakis (hydroxymethyl) phosphonium chloride with resorcinol (3). These tannages produced leather of saleable quality that had a high hydrothermal stability.

The availability of a research sample kindly supplied by the Shell Chemical Company† of an acrolein-formaldehyde condensation product (4) prompted an investigation of its tanning action in combination with resorcinol (5). For convenience, it will be referred to as AN/F. It is postulated to contain both hemi-

*Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

†The mention of firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.

acetal and acetal groups. The hemiacetal groups are unstable and revert readily to aldehyde groups in the pH range of the tanning process. These then react with resorcinol.

It will be shown that commercial quality leather can be produced. However, the work has more theoretical interest than practical value because of the nature of the procedure and cost of the chemicals.

EXPERIMENTAL

Procedure. Experimental tannages were carried out in the laboratory in a small drum using three domestic sheepskins or three New Zealand lambskins per run. The following is a typical procedure:

Sheepskin, pickled	100%
Water	100%
Sodium sulfate	10%
Sodium acetate	3%
Acrolein-formaldehyde condensate	6%
Resorcinol	2.5%
Sodium bicarbonate in feeds	4–5%
Washed	
Sulfuric acid	1 to 1 ½%
Washed	

Most of the water and all of the sodium sulfate and sodium acetate were mixed in a warmed drum. The skins were entered and depickled for 20 minutes. The pH of the liquor was then 4.7. The AN/F and resorcinol were added, and the drum was run for one hour. The pH remained at 4.7. The shrinkage temperature was 74°C. indicating some tanning action by the aldehyde polymer. The pH was raised gradually by the addition of four to five percent sodium bicarbonate in three portions until a pH of 7.8–8.0 was reached. Tanning was discontinued after four hours at this pH. After three hours at pH 7.8–8.0, a test was made for residual resorcinol. Sulfuric acid and formaldehyde were added to a small sample of the tanning liquor. A red precipitate indicated the presence of resorcinol. The test was usually negative. For the last hour of tanning the temperature was raised to 95–105°F. by cautiously running steam into the drum for one or two minutes in an attempt to duplicate the rise in temperature that occurs when tanning a large pack.

The total time of tanning was seven hours. The shrinkage temperature was 93–94°C. The skins were washed briefly and acidified with one to one and one-half percent sulfuric acid to a pH of 4.0–4.5. The shrinkage temperature increased two to three degrees after acidification. The skins were washed after acidification, treated with a disinfectant, and horsed to drain.

The tanned skins were sent to tanneries for processing into finished leather. Work glove leather was made from the domestic sheepskins and garment suede from the New Zealand lambskins.

Properties of the leather.—The color of the leather before dyeing was very light tan, and the leather darkened only slightly on aging. The work glove leather was full, round and mellow. The suede leather had a fine nap and was quite mellow.

The strength of finished leather was measured using ALCA-ASTM procedures (6,7). The average results were as follows:

Test	Work Glove	Suede
Tensile strength, PSI	2590	2520
Slit tear, lb. to tear	12	10
Ball burst, lb./in. thickness	1647	1595

These results compared favorably with measurements obtained on conventionally tanned sheepskins. The shrinkage temperature of the finished work glove leather was 90–92°C. and that of the suede 95–97°C.

The resistance of the leather to deterioration from perspiration was also evaluated using the solution described in the tentative ALCA-ASTM method, which is a modification of the Roddy, Lollar method (8).

The following synthetic perspiration solution was adjusted to pH 7.5:

Sodium chloride	9.0 g.
Urea	1.67 g.
Sodium lactate	86.0 g.
Sodium acid phosphate · 12 H_2O	0.165 g.
Distilled water to volume	1000 ml.

The 3″ x 3″ pieces of leather were soaked in the synthetic perspiration solution for one hour, then put into a container with 100 ml. of water, sealed to insure constant 100 percent humidity, and placed in an oven at 70°C. for 48 hours. Control pieces were soaked in a nine percent salt water solution for one hour. The leather was resistant to the conditions of the test, remaining mellow and soft with only slight shrinkage in area.

DISCUSSION

AN/F is a product resulting from the condensation of acrolein and formaldehyde. It is believed to exist in a hemiacetal structure. It is a 50 percent aqueous solution. No further information about its preparation or structure is available.

This has necessitated two assumptions as a starting point in this work. It is assumed that the molecular ratio of acrolein to formaldehyde is one to one and that two aldehyde groups are potentially available in each unit. These assumptions were used to calculate the ratio of AN/F to resorcinol. The total amount of chemicals was arbitrarily chosen to produce a leather with a shrinkage temperature of 90°C. or above. This is accepted as adequate for most commercial sheepskin leathers.

The influence of the mole ratio of AN/F to resorcinol on the shrinkage temperature of the leather, determined after tanning and acidifying to a pH of 4.0–4.5, is shown in Table I. The maximum shrinkage temperature obtained with AN/F alone was 82°C. Using two and one-half percent resorcinol and a ratio of one molecular equivalent of AN/F the shrinkage temperature was 80–82°C. The maximum shrinkage temperature obtained with this ratio and a high amount of chemicals was 88°C. When using a ratio of two parts of AN/F to one of resorcinol, a large amount of both chemicals did produce a shrinkage temperature of 97°C. However, the greater efficiency and economy of a ratio of three moles of AN/F to one of resorcinol is apparent in experiment 8 (Table I). In

TABLE I

INFLUENCE OF THE RATIO OF AN/F[1] TO RESORCINOL ON THE T_s[2] OF DOMESTIC SHEEPSKINS

Experiment No.	AN/F %	Resorcinol %	Ratio moles	T_s °C.
1	5	—	—	82
2	20	—	—	82
3	2	2.5	1:1	80–82
4	8	10	1:1	88
5	3	1.9	2:1	83
6	12	7.5	2:1	97
7	3.6	1.5	3:1	92
8	6	2.5	3:1	94–96
9	12	5	3:1	>100[3]
10	12	2.5	6:1	92–94

[1]Acrolein-formaldehyde condensation product.
[2]Shrinkage temperature.
[3]Five-minute boil.

previous work, using formaldehyde and resorcinol, this ratio has been shown to produce the best results (2). Six percent of AN/F and two and one-half percent of resorcinol gave a shrinkage temperature of 94–96°C. Larger quantities

of chemicals, using this ratio, produced sheepskin leather that did not shrink in boiling water in five minutes. The last experiment using six moles of AN/F to one of resorcinol indicates that there is no advantage in using a much higher ratio of AN/F to resorcinol.

It will be noted that only mildly alkaline conditions are described in the procedure. This is a necessary limitation since AN/F is decomposed by strong acids, and resorcinol is not reactive at an intermediate pH range. When the tanning was carried out at a higher final pH of 8.5 to 9.0, the shrinkage temperature was definitely lower.

Individual components and various combinations of formaldehyde, acrolein, and resorcinol have been evaluated under identical conditions as described in the tanning procedure. Formaldehyde alone produced leather with a shrinkage temperature of 85°C. after acidification. Acrolein alone gave a shrinkage temperature of 74°C. Acrolein and resorcinol gave poor results. The shrinkage temperature was 67°C. at the end of tanning at a pH of 7.8 and 74°C. after acidification to a pH of 4.0 to 4.5. This is the same as the final shrinkage temperature obtained with acrolein alone. A mixture of two and one-half percent resorcinol and equivalent quantities of acrolein and formaldehyde in a ratio of one mole of resorcinol to three moles of total aldehyde produced leather with a significantly lower shrinkage temperature; namely, 77°C. It appears that the presence of free acrolein interferes with the reaction of formaldehyde and resorcinol, possibly because of the addition of resorcinol to the carbon-carbon double bond in acrolein. AN/F was hydrolyzed with acid overnight, and the hydrolyzate was used alone and in combination with resorcinol, raising the pH gradually to 7.8–8.0, as before. The shrinkage temperature of the sheepskin tanned with the hydrolyzate alone was 83°C. With added resorcinol and tanning for the standard length of time the shrinkage temperature was only 86°C., and the resorcinol test was positive.

The tanning mechanism appears to be a Mannich-type reaction involving a compound containing very reactive hydrogen atoms; namely, resorcinol, an aldehyde and an amine. The amine is provided by the ε-amino group of the lysine residue of collagen and possibly by the guanidine group of the arginine residue. While the Mannich reaction was originally defined as taking place in acid solution, the definition has been broadened to include alkaline reactions. The leather is strong and mellow, which would indicate the formation of a relatively low molecular weight, linear polymer. Perhaps this is brought about by the termination of the polymerization through reaction with the protein. The acrolein-formaldehyde condensation product may contain more than two hemiacetal groups depending upon the length of the chain. This, together with the formation of larger molecules with resorcinol and the presence of a number of methylol groups on the resorcinol residue, would provide desirable spatial relationships and a number of sites for crosslinking.

SUMMARY

Resorcinol, in combination with a condensation product of acrolein and formaldehyde, produces good quality leather with a high hydrothermal stability and excellent perspiration resistance.

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