PERSPIRATION RESISTANCE OF LEATHER TANNED WITH TETRAKIS(HYDROXYMETHYL)PHOSPHONIUM CHLORIDE–RESORCINOL

ABSTRACT

Leather tanned with tetrakis(hydroxymethyl)phosphonium chloride (THPC) and resorcinol alone and retanned with other tanning agents has a high degree of perspiration resistance. The efficacy of a small amount of THPC-resorcinol followed by a retannage with a moderate amount of basic chromium sulfate is striking.

INTRODUCTION

One phase of the research program of this laboratory is concerned with the development, testing, and evaluation of new leathers having increased resistance to deterioration. Some leathers, such as those used in hat bands and in shoe insoles and uppers, deteriorate under adverse conditions because of poor resistance to perspiration. This is due to the detanning action of the constituents of natural perspiration, such as lactates, urea, and sodium and potassium salts.

The mechanism of deterioration varies with the type of tannage. Chrome-tanned leathers are degraded by the lactate ions which remove the chrome through chelation (1), while vegetable-tanned leathers are attacked by the alkaline materials and by urea. Leather is also degraded by moisture alone at body temperature when exposed over prolonged periods (2). Under these conditions the protein is gradually hydrolyzed. The degree of decomposition reflects the strength of the cross links established by the tanning agent. Improved leathers should result from the use of chemical agents that establish stable cross links within the protein.

Previous work by this laboratory has shown that retannage of vegetable-tanned insole leather with basic aluminum acetate increases the serviceability of the insoles about 70% (3). Recently our laboratory found that the glutaraldehyde tannage produces leathers with excellent perspiration resistance as judged by an accelerated perspiration test (4).

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A routine evaluation of this property on THPC-resorcinol–tanned sheepskins (5) indicated significant perspiration resistance. This prompted a more intensive investigation to determine the minimum quantities of THPC and resorcinol necessary, alone and in combination with other tanning agents, to impart perspiration resistance.

EXPERIMENTAL

The following modification of the method described by Roddy and Lollar (6,7) was used to determine perspiration resistance.

Perspirant solution

	g/l
Urea, cryst.	1.67
Sodium lactate, 60% syrup	100.0
Disodium phosphate, 12 H_2O	0.417
Sodium chloride	9.75

Adjusted to pH 7.0 to 7.1 with ammonium carbonate or lactic acid.

Perspiration test method.—Two- by three-inch leather samples were soaked with occasional flexing for 2 hr. in the perspirant solution. Large, rectangular, heat-resistant glass jars and covers were preheated at 70°C. The leather samples were hung on glass rods within the jars which contained 100 ml. of water at 70°C. The jars were sealed tightly with plate glass covers and placed in the oven at 70°C. for 48 hr. The leathers were removed, air-dried at room temperature, then examined for area change, discoloration, and stiffness. Two- by three-inch leather samples were tested for the effect of heat (70°C.) and high humidity (100%) by using distilled water in place of the perspirant solution in the above test. A planimeter was used to measure the area of the leather before and after testing. The percent area loss or gain was calculated.

Perspiration resistance of leathers.—Domestic, New Zealand, Iranian, and Syrian sheepskins and Iranian goatskins were tanned with THPC, with THPC and resorcinol, and with THPC and resorcinol followed by chrome or other tanning agents. They were fatliquored and processed into grain garment, suede, slipper, and work glove leathers by commercial tanners. The finished leathers were examined for perspiration resistance. The results are given in Fig. 1 and in Tables I, II, and III.

RESULTS AND DISCUSSION

THPC-resorcinol–tanned leathers.

Domestic sheep.—Sheepskins tanned with THPC as the only tanning agent were not resistant to perspiration. However, skins tanned with the polymers formed by the reaction of THPC and resorcinol possessed excellent perspiration resistance when adequate amounts of the tanning agents were

TABLE I

PERSPIRATION RESISTANCE OF THPC-RESORCINOL LEATHER

Tannage		Ts			Water Control			Perspiration		
THPC %*	Resorcinol %*	Depickled °C.	Tanned °C.	ΔTs °C.	Area Loss %	Discoloration†	Stiffness†	Area Loss %	Discoloration†	Stiffness†
Domestic Sheep										
0.87	0.5	50	78	28	16	+	++	60	+	++++
1.73	1.0	50	83	33	4	+	+	3	+	+
2.6	1.5	50	84	34	1	0	+	5	+	+
3.5	2.0	50	89	39	2	+	+	0	+	+
4.3	2.5	50	91	41	5	+	+	3	+	+
5.6	3.0	50	98	48	4	+	+	5	+	+
New Zealand Sheep										
0.87	0.5	52	81	29	8	0	++	7	0	++
1.73	1.0	52	84	32	3	+	+	3	+	+
5.6	3.0	52	96	44	7	0	0	4	+	0
Iranian Sheep										
1.73	1.0	52	82	30	12	++	+	62	++++	++++
5.6	3.0	52	95	43	7	+	0	1	+	0

*Percent based on drained pickled weight of skins.
† + slight; ++ moderate; +++ severe; ++++ very severe.

TABLE II

PERSPIRATION RESISTANCE OF THPC-RESORCINOL LEATHER RETANNED WITH CHROME

Tannage			Ts			Water Control			Perspiration		
THPC %*	Resorcinol %*	Chrome %*	Depickled °C.	Tanned °C.	ΔTs °C.	Area Loss %	Discoloration†	Stiffness†	Area Loss %	Discoloration†	Stiffness†
Domestic Sheep											
—	—	3.0	50	87	37	2	0	+	70	+	++++
0.87	0.5	3.0	50	>100	50+	3	+	+	0	+	+
—	—	4.0	50	92	42	3	+	+	74	++	++++
0.43	0.25	4.0	50	>100	50+	2	+	+	2	+	+
1.73	1.0	4.0	50	>100	50+	3	0	+	3	+	+
New Zealand Sheep											
0.87	0.5	4.0	52	97	45	7	0	+	8	+	++
1.73	1.0	4.0	52	>100	48+	12	+	+	7	+	+
Syrian Sheep											
—	—	3.0	46	87	41	7	+	+	79	++++	++++
0.43	0.25	4.0	46	98	52	10	+	+	71	++++	++++
Iranian Sheep											
—	—	4.0	52	94	42	3	+	+	80	++++	++++
0.87	0.5	3.0	52	95	43	8	+	0	9	+	+
Iranian Goat											
0.87	0.5	3.0	48	94	46	7	+	+	7	+	+

*Percent based on drained pickled weight of skins.
†+ slight; ++moderate; +++ severe; ++++ very severe.

TABLE III

PERSPIRATION RESISTANCE OF THPC-RESORCINOL LEATHER RETANNED WITH MISCELLANEOUS TANNING AGENTS

Tannage			Ts			Water Control			Perspiration		
THPC %*	Resorcinol %*	Other Tanning Agent* %	Depickled °C.	Tanned °C.	ΔTs °C.	Area Loss %	Discoloration†	Stiffness†	Area Loss %	Discoloration†	Stiffness†
New Zealand Sheep											
0.87	0.5	8.0[a]	52	82	30	3	0	0	0	+	+
0.87	0.5	8.0[a]	52	80	28	3	+	+	+7	+	+
0.87	0.5	10.0	52	89	37	4	+	0	+6	+	+
0.87	0.5	7.4[b]	52	90	38	3	0	0	1	+	+
0.87	0.5	3.4[c]	52	86	34	3	0	+	+3	+	0
0.87	0.5	6.0[d]	52	82	30	4	0	+	+2	+	+
0.87	0.5	6.0[e]	52	81	29	3	0	0	+2	+	0

*Percent based on drained pickled weight of skins.

†+ slight; ++moderate; +++ severe; ++++ very severe.

a. basic zirconium sulfate; b. basic aluminum acetate; c. methylolmelamine; d. powdered wattle extract· e. powdered canaigre extract.

ACCELERATED PERSPIRATION TEST SHEEPSKINS

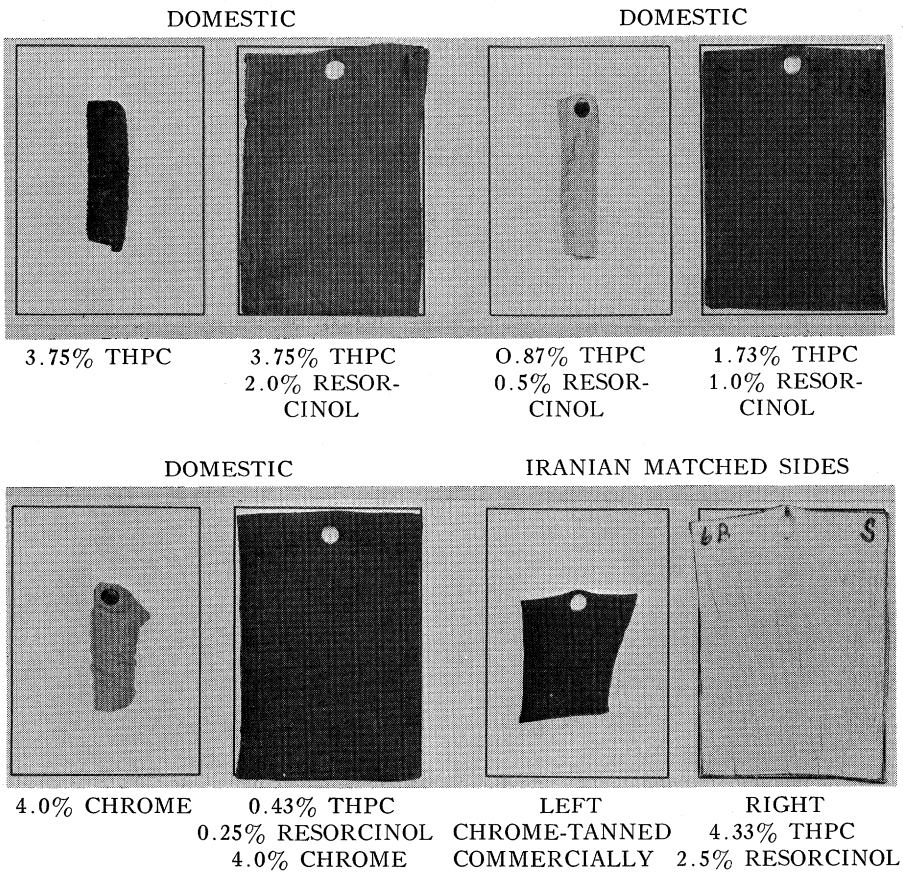

FIGURE 1—Photograph of perspiration test specimens.

used. A skin tanned with 3.75% THPC alone shrank and gelatinized severely, whereas the skin tanned with 3.75% THPC and 2.0% resorcinol remained in good condition. These results are shown in Fig. 1.

Skins tanned with 0.87% THPC and 0.5% resorcinol failed in the perspiration test, while those tanned with 1.73% THPC and 1.0% resorcinol and with higher amounts resisted deterioration with only slight area loss (3–5%), discoloration, and increase in stiffness (Fig. 1 and Table I). Leathers that passed the test had an increase in shrinkage temperature (Δ Ts) during tanning of 33 °C. or more above that of the pickled stock. A relatively low level of THPC and resorcinol is effective in producing perspiration-resistant leather.

New Zealand sheep.—Skins tanned with as little as 0.87% THPC and 0.5% resorcinol and with a Δ Ts of 29°C. passed the perspiration test with only slight area loss (7%), discoloration, and a moderate increase in stiffness. The fact that New Zealand sheep passed the test at the 0.87% THPC—0.5% resorcinol level and domestic sheep did not is probably due to the higher quality and higher original shrink temperature of the New Zealand skins.

Iranian sheep.—These leathers showed poorer perspiration resistance than the domestic and New Zealand skins, failing the test at the 1.73% THPC—1.0% resorcinol level. The 5.6% THPC—3.0% resorcinol leather was excellent, with very slight area loss and discoloration.

In another experiment six skins were cut down the backbone. The left sides were tanned commercially with a relatively low amount of basic chromium sulfate, and the right sides were tanned with 4.33% THPC and 2.5% resorcinol. The THPC-resorcinol leather showed excellent perspiration resistance, while the chrome-tanned leather failed (Fig. 1).

THPC-resorcinol–chrome leathers.

Domestic sheep.—Skins tanned with small amounts of THPC and resorcinol and retanned with no more than half of the usual amount of basic chromium sulfate produced leathers with excellent perspiration resistance (Table II). For example, leathers tanned with as little as 0.43% THPC and 0.25% resorcinol and retanned with 4.0% chrome passed the test with only slight area loss (2%), discoloration, and increase in stiffness. Chrome-tanned control leathers tanned with 3.0% or 4.0% chrome alone failed the test completely with 70–74% area loss. This difference is illustrated by the perspiration test specimens shown in Fig. 1. The protection afforded by the small amount of the polymeric tannage in combination with a low chrome retannage is striking.

New Zealand sheep.—Perspiration resistance was about the same as that of domestic sheep. Skins tanned with 0.87% THPC and 0.5% resorcinol and retanned with 4.0% chrome passed the test with only slight area loss (7%), discoloration, and increase in stiffness.

Syrian sheep.—Although domestic skins tanned with 0.43% THPC and 0.25% resorcinol and retanned with 4% chrome had good perspiration resistance, these same quantities of chemicals did not protect Syrian skins even though the shrink temperature was 98°C.

Iranian sheep.—Skins tanned with 0.87% THPC and 0.5% resorcinol and retanned with 3.0% chrome had moderate perspiration resistance but were not as good as domestic skins tanned with the same amounts of chemicals.

Iranian goat.—These leathers were approximately the same as the Iranian sheep in perspiration resistance.

Miscellaneous retannages.—New Zealand lambskins tanned with 0.87% THPC and 0.5% resorcinol were retanned with one of the following: basic

zirconium sulfate (8.0% and 10.0% Zircotan N*), basic aluminum acetate (7.4%), methylolmelamine (3.4%), powdered wattle extract (6.0%), powdered canaigre extract (6.0%). These passed the perspiration test with little or no area loss or discoloration and with little or no increase in stiffness. Some showed a slight gain in area (Table III). This is excellent perspiration resistance when it is considered that the shrink temperature of four of the combination tannages was 80°–82°C.

The accelerated perspiration test is drastic in view of a temperature of 70°C. and a humidity of 100%. It is well known that shrinkage is a function of time as well as temperature. In the above tannages no correlation was found between skrink temperature and ability to pass the perspiration test. Some leathers with shrink temperatures of 80°–81°C. were satisfactory, while others with shrink temperatures as high as 94°–98°C. failed. Perspiration resistance appears to depend mainly upon the specific kind and amount of tanning agent used and to a lesser degree upon the physical structure, quality, and original shrink temperature of the raw stock.

In every instance where protection was obtained, the leather remained mellow and flexible with only a slight increase in firmness. The high resistance of the THPC-resorcinol leather to moist heat and perspiration is thought to be due to the introduction of stable cross links into the collagen by the formation of covalent bonds. *In situ* polymerization probably serves to produce compounds with advantageous spatial relationships for the formation of cross links.

SUMMARY

Leathers tanned with tetrakis(hydroxymethyl)phosphonium chloride and resorcinol or with small quantities of these chemicals in combination with other tanning agents showed excellent resistance to deterioration by an accelerated perspiration test.

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