TECHNICAL NOTES

WASHABILITY OF GLUTARALDEHYDE-CHROME TANNED GARMENT AND GLOVE LEATHERS

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INTRODUCTION

One of the aims of the leather industry is the development of washable leathers that require little special attention. The term "washable leather," as used here, means a leather that can be immersed in warm to moderately hot water and washed with soap or detergent in a manner, for example, as recommended for woolen fabrics. Such leather could compete more readily with substitutes in many ways but especially in low maintenance cost.

There does not seem to be much in the recent literature on washable leather other than advertising claims. The test methods (1, 2) for washable leather in England and the United States are concerned entirely with the fastness or transfer of color. For washable leather, it would seem reasonable to require that the tannage and lubrication, as well as the color, offer relatively good resistance to standard washing conditions. This resistance must continue during repeated wash and dry cycles, so that the leather may retain a satisfactory shrink temperature, appearance and handle.

Research and practical application of wash-fast leather dyes have been reported (3, 4, 5). The problem of wash-proof fatliquors may not be difficult to solve (6). In fact, some of the data in this report indicate that fatliquors and lubricants are not as readily removed during washing as may happen in dry cleaning (7). Some dryness usually develops on the surface of the washed leather after several washes which should be corrected by surface application of a little fatliquor or softening agent (6, 7).

No special fatliquors were used in the tests reported here. The tanneries that processed the skins, after tannage in the laboratory, used the type of fatliquor they normally use for such skins.

This report concerns itself mainly with one of the major requirements listed above: the effect of repeated wash-dry cycles on the shrink temperature (Ts) of leather. Here, the Ts is considered a measure of the stability of the tannage. If the drop in Ts can be retarded significantly, a given leather may be considered a suitable substrate for the production of washable items. However, this must also take into consideration the expected drop in Ts as leather ages.

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EXPERIMENTAL

Garment Type Leathers

The work described here was designed to compare the effect of glutaraldehyde retannage on the launderability of three types of garment leathers. These included two suede types and one grain type prepared as follows:

Glutaraldehyde Retannage of Chrome-Vegetable Suede. Ten commercially tanned New Zealand lamb skins (see Table I) were used for this series of tests. These skins had been chrome-tanned, vegetable retanned, and were intended for garment suede. They were removed from processing in the tannery prior to fatliquoring. Eight of these skins were retanned in the laboratory with glutaraldehyde, as follows: The skins were placed in a small drum containing a 1:1 float plus 10 percent glutaraldehyde (as 25 percent commercial solution) at about 50°C. (120°F.). After running for one hour at pH 3.9, sodium bicarbonate (one percent skin weight as received) was added to bring the pH up to 4.4. This pH was maintained during the retannning period of six hours. Afterwards the skins were washed in running water for a half hour and then horsed overnight under a polyethylene cover. Ts specimens withstood a 3-minute boil test before and after the glutaraldehyde retannage. The retanned skins were returned to the tannery for fatliquoring and processing into suede along with the two not retanned, reserved as controls.

Glutaraldehyde Retannage of Chrome-Tanned Suede. For the second series of tests eight commercially chrome-tanned lambskins were retanned with glutaraldehyde as described above (Table II). These skins were intended for suede but were removed from processing in the tannery before the vegetable retan and fatliquoring steps. Presumably, these skins were similar to those mentioned above (and in Table I) except for the vegetable retannage. The shrink temperatures of the skins were 105–106°C. (in water, using pressurized equipment [11]) before and after the glutaraldehyde retannage. These eight skins were then returned to the tannery for fatliquoring and processing into suede along with five others that were sent back as received.

Glutaraldehyde Retannage of Chrome-Tanned Grain Garment Leather. Eight commercially chrome-tanned Turkish sheep skins were retanned with glutaraldehyde as described for suede leather above (Table III). The quantity of glutaraldehyde used for these skins was the same as that used for suede. In this case, however, the chrome stock in equilibrium with the retanning solution had a pH of 5.1. During the early stages of the retannage small amounts of acetic acid were added to reduce the pH to 4.3. The shrink temperature of the retanned skins was 99°C. compared to 97°C. for the chrome-tanned skins as received. The eight retanned skins were sent to the tannery, along with four others that

TABLE I

ANALYSIS OF SUEDE LEATHER BEFORE AND AFTER WASHING

(a) Chrome-Vegetable Tannage; (b) Chrome-Vegetable Tan, Glutaraldehyde Retannage

Wash	Ts, °C., After Washing*		Ash, %†		Cr (as Cr_2O_3), %†		$CHCl_3$ Extractable, %†		Sodium‡		Calcium‡		Magnesium‡	
Cycle	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
0	108	110	5.40	6.34	3.56	3.43	10.89	11.99	0.099	0.079	0.36	0.16	0.11	0.07
1	107	107	5.92	4.85	3.54	3.48	14.25	12.99	.081	.093	3.30	1.46	.70	.43
2	105	106	—	—	—	—	—	—	—	—	—	—	—	—
3	104	105	—	—	—	—	—	—	—	—	—	—	—	—
4	104	105	6.73	6.88	3.40	3.42	17.55	15.34	.070	.070	12.45	8.06	.87	.64
5	100	104	—	—	—	—	—	—	—	—	—	—	—	—
6	100	103	—	—	—	—	—	—	—	—	—	—	—	—
7	98	103	7.28	6.49	3.29	3.28	17.36	17.42	.070	.059	14.98	14.12	.73	.70

*When received from the tannery the Ts of the ten leathers varied from 106–110°C.

†Values on moisture-free basis.

‡% element in ash, analysis by means of Perkin-Elmer Atomic Absorption Spectrophotometer Model 303.

TABLE II

ANALYSIS OF SUEDE LEATHER BEFORE AND AFTER WASHING

(a) Chrome Tannage; (b) Chrome Tan, Glutaraldehyde Retannage

Wash	Ts, °C., After Washing*		Ash, %†		Cr (as Cr_2O_3), %†		$CHCl_3$ Extractable, %†		Sodium‡		Calcium‡		Magnesium‡	
Cycle	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
0	103	103	5.76	9.13	4.59	4.46	9.21	10.57	0.116	0.071	1.72	0.22	0.04	0.06
1	95	99	7.25	9.33	4.33	4.38	11.99	10.05	.118	.117	.97	1.40	.07	.10
2	89	94	—	—	—	—	—	—	—	—	—	—	—	—
3	87	93	—	—	—	—	—	—	—	—	—	—	—	—
4	87	92	6.78	9.82	4.11	4.02	16.70	17.48	.111	.045	10.24	7.77	.19	.24
5	85	92	—	—	—	—	—	—	—	—	—	—	—	—
6	86	90	—	—	—	—	—	—	—	—	—	—	—	—
7	84	90	9.15	9.45	3.90	3.93	18.45	18.22	.076	.121	15.11	12.68	.24	.30

*When received from the tannery the Ts of the thirteen leathers varied from 103–105°C.

†Values on moisture-free basis.

‡% element in ash, analysis by means of Perkin-Elmer Atomic Absorption Spectrophotometer Model 303.

TABLE III

ANALYSIS OF GRAIN GARMENT LEATHER* BEFORE AND AFTER WASHING

(a) Chrome Tannage; (b) Chrome Tan, Glutaraldehyde Retannage

Wash	Ts, °C., After Washing†		Ash, %‡		Cr (as Cr_2O_3), %‡		$CHCl_3$ Extractable, %‡		Sodium**		Calcium**		Magnesium**	
Cycle	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
0	90	92	5.92	5.60	4.23	3.91	25.47	25.55	3.29	3.69	0.19	0.16	0.05	0.05
1	87	92	5.59	5.33	4.20	4.21	28.61	24.78	.07	.125	4.00	2.74	.12	.14
2	86	92	—	—	—	—	—	—	—	—	—	—	—	—
3	86	90	—	—	—	—	—	—	—	—	—	—	—	—
4	83	89	6.13	5.59	4.03	3.59	25.00	25.32	.082	.118	5.95	7.50	.16	.96
5	81	88	—	—	—	—	—	—	—	—	—	—	—	—
6	79	88	—	—	—	—	—	—	—	—	—	—	—	—
7	78	86	7.15	7.07	3.92	3.68	31.46	32.43	.054	.058	10.68	14.54	.58	.65

*Turkish Sheepskin.

†When received from the tannery the Ts of the twelve leathers varied from 92–94°C.

‡Values on moisture-free basis.

**% element in ash, analysis by means of Perkin-Elmer Atomic Absorption Spectrophotometer Model 303.

were sent as received, for fatliquoring and processing into grain garment leather. Upon return from the tannery, it was noticed that the Ts of the leather had dropped 5°C. in both cases

Washing Tests

The control leathers (not retanned with glutaraldehyde) were cut into quarters. One of these was reserved for comparison as an unwashed control and the others were included with the batch of seven whole skins from the experimental tannage that were subjected to laundering. Of the retanned leathers one whole skin was retained as an unwashed control for future evaluations and comparisons.

The finished leathers were laundered by washing in an agitator type washing machine for ten minutes using 30 liters of water at 50°C. and 15 grams of Ivory Soap† flakes. Then the leather was rinsed three times (5 minutes each time, with agitator action) using 30 liters of water at 50°C. for each rinse. Finally, all the leather was hand squeezed and hung up to air-dry overnight at room temperature. The next day a quarter skin sample of the control (not retanned with glutaraldehyde) and a full skin were set aside. All the others were put through another wash cycle as described above. These were later air-dried again overnight and a second full skin and quarter skin were removed from the test. The wash-dry cycles were continued and repeated until all of the full skins and quarter skins were removed. Because of the reduced number of samples in the 5th, 6th and 7th wash cycles, the quantities of water and soap used were cut in half for both the washing and the rinsing.

Cabretta Glove Leather

Tests were run on the comparative washability of three Cabretta leathers as measured by shrink temperatures. These leathers differ from those reported previously (9) in that the skins were not prebuffered overnight, and they were tanned for only seven hours instead of 24. Three groups (A, B and C) of pickled Cabretta, six skins each, were tanned in the laboratory, as outlined in Table IV. The tanned skins were sent to a tannery for fatliquoring and processing with a commercial pack.

Washing Tests

The leather specimens of each group were washed according to the specifications of Procedure B, ASTM Designation: D2096-62T (2). The only variation from the procedure was that four specimens were washed instead of three, and thus there were four wash cycles instead of three. Additional soap solution was used in proportion. Table V shows the changes in Ts during the wash tests.

†Mention of brand names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.

TABLE IV

TANNING PROCEDURES FOR CABRETTA GLOVE LEATHERS

	(A) Glutaraldehyde	(B) Glutaraldehyde	(C) Chrome
	Alone	Simultaneous with chrome	Alone
Pickled Cabretta skins, %[a]	100	100	100
Water	100	100	100
Glutaraldehyde (25% solution), %	12	12	—
Sodium Chloride, %	6	6	6
Tanolin R,[b] %	—	6	6
Drum ½ hr., pH	2.0	2.2	2.1
with heat lamp., temp. °C.	38	38	40
Add: sodium formate, %	5	4	4
Drum 2 hrs., pH	3.8	3.4	—
Add: sodium bicarbonate, %	5	½ every[c] half hr.	½ every[c] half hr.
pH	7.5	4.1	4.1
Drum with heating, hrs.	5-½	3	3
Drained, acidified			
Formic acid, %	3	—	—
Water, %	100	—	—
Drained, and washed, min.	15	30	30
Ts, °C.	81	105	96

[a]Percentages are on drained "blue" weight.

[b]Allow time, before starting the tannage, to dissolve Tanolin R in approximately one half the water listed. The solution time is shortened by heating. The solution is subsequently cooled to 50°C. before adding it to the tanning drum.

[c]One half percent feed of sodium bicarbonate was added every half hour until pH reached 4.1.

TABLE V

EFFECT OF WASHING ON Ts OF CABRETTA GLOVE LEATHER

Tannage	Ts, °C., After Wash Number				
	0	1	2	3	4
(A) Glutaraldehyde	72	75	75	74	74
(B) Glutaraldehyde-Chrome	88	87	81	78	77
(C) Chrome	87	70	66	58	55

DISCUSSION OF RESULTS

The work described here confirms the tendency for a glutaraldehyde retannage of chrome-tanned stock to retard the drop in shrink temperature during repeated wash cycles (8, 9, 10). In Table I, the Ts for a chrome-vegetable suede dropped, after seven wash cycles, from 108°C. to 98°C. Similar skins retanned with

glutaraldehyde dropped in Ts from 110°C. to 103°C. For suede leather such as above, but with no vegetable retan (Table II), the chrome-tanned stock dropped from 103°C. to 84°C. Glutaraldehyde retannage of this stock dropped from 103°C. to 90°C. after seven wash cycles. In the case of chrome garment leather (Table III), the Ts dropped from 90°C. to 78°C., whereas similar leather, retanned with glutaraldehyde, dropped from 92°C. to 86°C. All shrink temperatures over 100°C. were determined in water under pressure (11).

The appearance of the chrome-glutaraldehyde leathers held up very well throughout the seven wash cycles. There was no appreciable change in the nap of the suede.

After several washes, the straight chrome suede developed increasing surface harshness, noticeably more than the other leathers tested.

The appearance of the chrome-vegetable suede remained quite good throughout the seven wash cycles. The skins of this type that were retanned with glutaraldehyde were very good also. These seemed to be a little softer after the later wash cycles. The difference, however, was not great.

As expected from previous experience, the chrome-tanned grain leather began to develop a poor appearance and feel after the second wash cycle. The glutaraldehyde-retanned grain leather, however, retained its good appearance and pleasing characteristics throughout the seven wash cycles and compared favorably with an unwashed specimen.

The build-up of chloroform-soluble material shown in the tables is of interest. It should be noted that the values shown in the tables are for specific skins (a different skin for each wash cycle) and that such values can vary easily 2 to 3 percent from other skins treated in a similar manner. The fact that these values increase with additional wash cycles, in spite of skin variations, would indicate a definite pickup of fatty materials (chloroform extractables). This increase is caused by a combination of the following factors:

(a) The pickup of calcium and magnesium soaps (mostly calcium) which is formed by the relatively hard water (180 ppm total hardness) used in these wash tests. (See last two columns in Tables I, II and III.) The literature (12) indicates that calcium oleate is soluble in boiling chloroform, and that calcium palmitate is slightly soluble under the same conditions. Analysis at our Laboratory of the type of soap used in this test has shown that the fatty acids consist of almost one half oleic acid and over a fourth palmitic acid. Under the conditions of Soxhlet extraction, these materials would be extracted with the fats and oils in the leather. Thus the value for chloroform extractables would be augmented each time the samples were washed.

(b) Fatty acids are formed by neutralization of soap by acid in the skin and perhaps by ion exchange reactions involving the chrome-tanning complex in the

leather. The values for Cr (as Cr_2O_3) shown in the tables remain quite constant for seven wash cycles. However, the ash value increases as the wash cycles progress. Apparently, this build-up is not due to unrinsed soap because there is no parallel increase in sodium (sixth column, each table). Here again, the higher values are probably due to calcium and magnesium soaps formed during the wash cycles and held by the leather.

When reading the data in Tables I, II, III and V, it should be realized that the wash temperature used in these tests is much higher than that which would be recommended for washing leather at home or commercially. We have observed that the effect of this wash test on the Ts is much more drastic than when milder washing temperatures are used. For this reason, the development of the new "cold-water" detergents should be of interest in prolonging the life of washable leathers. This assumes, however, that the components of these "cold-water" detergents do not contain ingredients detrimental to leather or to the softening and finishing agents incorporated into the leather by the tanner.

In testing the Cabretta glove leather, we were not concerned with colorfastness or color transfer since these test leathers were not dyed. The Ts, appearance and feel of the leather were of most interest. The chrome-tanned leather (C) (Tables IV and V) began to change noticeably after the second wash cycle. It began to change in shape and feel with obvious shrinkage. The glutaraldehyde and glutaraldehyde-chrome specimens (A), (B), (Tables IV and V) remained soft and pleasing. There was not much change in physical shape or dimensions; also, the shrink temperature did not drop drastically.

The retention of these desirable properties encouraged the practical test of this type of leather (glutaraldehyde-chrome) recently described (13). In that test, a group of golfers used gloves made from the leather for a 6 to 8 month season. The perspiration resistance, washability, and "feel" of the gloves throughout the season met with their unanimous approval.

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