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THE ACTION OF PERSPIRATION ON LEATHER*

PART II. THE INFLUENCE OF RETANNAGE AND PRETANNAGE WITH SYNTANS AND VEGETABLE TANNING EXTRACTS ON THE RESISTANCE OF CHROME LEATHER TO PERSPIRATION*

ABSTRACT

Chrome leather is slowly detanned by the lactate ions present in perspiration. The possibility of increasing the stability of chrome leather to lactate by forming an additional link between the chrome complex and the hide protein has been examined.

Pretannage or retannage with a variety of syntans had no effect on the extraction of chrome or the fall in shrinkage temperature resulting from treatment in sodium lactate solutions. Vegetable tans, e.g., mimosa, sulfited quebracho, and myrobalans, however, caused an appreciable decrease in both the chrome extracted and the fall in shrinkage temperature. Resistance increased with the degree of vegetable tannage, reaching an optimum when the leather contained about four parts fixed tan for every one part of chrome (Cr_2O_3).

There was little to choose between the three tanning materials tested, and pretannage and retannage were equally effective. On the whole pretannage was preferred as higher initial chrome contents and shrinkage temperatures are more readily obtained, and distribution of the vegetable tan through the leather is more even.

The findings offer a partial explanation of the good resistance of semichrome and chrome retan leathers in wear.

INTRODUCTION

Chrome leathers have generally been found to be resistant to the action of moist heat (1–3). The chrome, however, is slowly extracted by the lactate ions in perspiration (4), and as the chrome content and shrinkage temperature are reduced the leather becomes increasingly susceptible to damage (5).

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It has been shown that the system leather-sodium lactate solution behaves similarly to that of a cation exchange resin in a solution of metallic cations, and of anions capable of complexing with these. At equilibrium the chrome is distributed between the skin and solution according to the number of groups present in each phase with which it is able to coordinate and its relative affinity for these (4).

An appreciable amount of the chrome present in chrome leather is thought to be coordinated with only one carboxyl group (unipoint fixation) (6). If an additional link between these complexes and the protein could be formed, greater stability to lactate should result. This might be done by means of a compound capable of coordinating with chrome and also of reacting with the protein. The possibility of using sulfophthalic acid was suggested by Gustavson (7) some years ago but has not found much use in practice. Other polyfunctional compounds which might serve this purpose are syntans and natural tannins, i.e., compounds containing several acidic or hydroxyl groups.

The effect of pretannage or retannage with a selection of such compounds on the stability of chrome leather has been investigated. Since resistance to moist heat appears to decrease progressively with decrease in chrome content (5), the initial chrome content as well as the resistance to extraction by lactate is an important factor, and the effect of the pretannage and retannage on the chrome content as well as on the stability of the fixed chrome has also been considered.

EXPERIMENTAL

Preparation of samples.—Commercial degreased pickled hair sheepskins were used for the majority of the experiments.

Pretannage.—Pieces of pelt about 30 g. in weight were brought to the required pH by drumming in 4% sodium chloride solution with the addition of sodium bicarbonate. The pieces were drained and then drummed in a 600% float of 2.5% w/v solutions of the test substances (15% test substance or vegetable tan extract on drained weight). For further details see Table I. After treatment the samples were drained, given a short pickle in 3% sodium chloride and sulfuric acid to bring the pH to 3.0, and then tanned in a 200% float of 33% basic chrome sulfate liquor containing 2% Cr_2O_3 and 3% sodium sulfate. After 16 hours the liquors were basified to pH 3.5 with sodium bicarbonate. The leather was drained overnight and air-dried.

Retannage.—The pelt was repickled and chrome-tanned as described above. After draining and rinsing, pieces of the chrome leather were treated with the various test substances under the same conditions as for pretannage. They were then rinsed and air-dried.

Samples of commercial crust chrome leather were also retanned with various amounts of mimosa and myrobalans. In these experiments the leathers were

TABLE I

DESCRIPTION AND METHOD OF APPLICATION OF TEST SUBSTANCES

Tans	Description	Method of Application
Syntans		
A	Cresol and cresol sulfonic acid—formaldehyde	pH 3.0
B	Similar to A but also contains resins derived from dihydroxyphenols and formaldehyde	pH 3.5
C	Cresol—formaldehyde + monomethylamine—amphoteric	Started at pH 3.5 Completed at pH 5.0
D	Dihydroxy—diphenylsulfone—formaldehyde—contains hydroxymethyl groups	In suspension in 1% $NaHCO_3$ at pH 7–8
E	Naphthalene—phenol sulfone	In 1% $NaHCO_3$ as in D
F	Resorcinol—formaldehyde—anionic	pH 3.5
G	Resorcinol—formaldehyde—amphoteric	Started at pH 3.5 Completed at pH 5.0
H	Resorcinol—formaldehyde—low molecular weight	Started at pH 3.5 Completed at pH 4.5
Vegetable Tans		
Quebracho	Lightly sulfited extract containing 36% tan, 45% total solids	pH 3.0
Mimosa	Lightly bleached with sulfite containing 30% tan, 40% total solids	pH 3.0
Myrobalans	Extract containing 25% tan, 40% total solids	pH 3.0
Lignosulfonic Acid		pH 3.0
Sulfophthalic Acid		pH 3.5

wet-back and retanned in a 500% float (on wet weight) for 24 hours with intermittent drumming.

Extraction with lactate.—Leathers were extracted with 5% w/v sodium lactate solutions containing 5% sodium chloride at pH 5.0, for 4 days at 50°C., using 25 ml. solution per g. leather (4).

Methods of analysis.—Chrome was determined by wet oxidation with perchloric acid (8), and water solubles and fixed tan by the S.L.T.C. Official Methods (9).

Shrinkage temperatures were determined in 75% glycerol-water mixtures as recommended by ALCA (10).

RESULTS

The effect of retannage with the various test substances is shown in Table II.

In all cases the chrome content was decreased by about 50%, and the shrinkage temperature was reduced. This suggests that all the compounds complex with chrome, probably by reason of the hydroxyl or carboxyl groups they contain, and that this leads, as with lactate, to breakdown of the protein-chrome complex and the formation of soluble chromium compounds.

With vegetable tanning solutions the carboxylic acids of the nontan fraction are probably at least partially responsible for this "detannage". These three leathers had in fact the lowest chrome contents of the series, but their shrinkage temperatures were still relatively high.

On extraction with sodium lactate solutions the majority of the leathers lost 65–80% of their chrome, compared with 80% for the control which had received no pretannage, and their shrinkage temperatures fell to values in the range 70° to 80°C. Since the chrome contents had already been reduced by retannage, the final chrome contents of most of these leathers were less than that of the control. The leathers retanned with mimosa, sulfited quebracho, and myrobalans, however, behaved differently; only 15–30% of the chrome was extracted, and what is perhaps more important, the falls in shrinkage temperature were relatively small. In spite of the reductions in chrome content and shrinkage temperature during retannage the final chrome contents of these leathers after lactate extraction were greater than that of the control and their shrinkage temperatures some 15°–30° higher. The leather retanned with the resorcinol-formaldehyde resin H and the naphthalene-phenol-sulfane Syntan E showed some improvement over the control with respect to chrome lost, but not shrinkage temperature.

Also shown in Table II are the corresponding results for samples pretanned with the same compounds and then chrome-tanned. In all cases the chrome contents and shrinkage temperatures after the completion of tannage were higher than in the first series and, in general, were similar to that of the pelt tanned directly with chrome.

Pretannage with Syntans C and E and sulfophthalic acid slightly increased the chrome content compared with the control, and the vegetable tans, syntan B, and lignosulfonic acid slightly decreased the shrinkage temperature.

TABLE II

EFFECT OF PRETANNAGE AND RETANNAGE WITH SYNTANS AND VEGETABLE TANS ON THE RESISTANCE OF CHROME LEATHER TO LACTATE

	Original Leather		After Treatment in Lactate Solutions			
	Cr_2O_3 g. per 100 g. air-dry leather	Ts °C.	Cr_2O_3 g. per 100 g. air-dry leather	% Cr_2O_3 Extracted	Ts °C.	Fall in Ts
RETANNAGE						
None	3.52	112	0.62	80	78	32
Syntan A	1.79	98	0.27	80	70	28
B	1.73	100	0.48	75	72	28
C	1.94	99	0.48	75	79	20
D	1.76	91	0.61	70	70	21
E	1.44	82	0.60	60	70	12
F	1.96	102	0.45	75	72	30
G	1.76	100	0.35	80	79	21
H	1.54	105	0.84	50	78	27
Quebracho	1.44	106	0.90	30	92	14
Mimosa	1.54	106	1.04	30	106	0
Myrobalans	1.49	99	1.26	15	92	7
Lignosulfonic acid	1.50	96	0.17	80	73	26
Sulfophthalic acid	1.61	96	0.23	85	72	25
PRETANNAGE						
None	3.52	112	0.62	80	78	32
Syntan A	3.47	110	0.40	88	79	31
B	2.93	107	0.30	80	81	26
C	4.25	117	0.46	80	79	38
D	3.27	115	0.45	80	78	37
E	5.12	115	1.00	80	86	30
F	3.84	112	0.40	80	79	33
G	3.56	111	0.27	80	76	35
H	3.47	113	0.44	80	80	33
Quebracho	3.64	102	1.60	60	96	8
Mimosa	3.19	104	1.28	60	98	6
Myrobalans	3.43	105	1.94	40	104	1
Lignosulfonic acid	3.49	106	0.53	88	75	31
Sulfophthalic acid	4.16	111	0.40	80	78	33

TABLE III

EFFECT OF RETANNAGE AND PRETANNAGE WITH VEGETABLE TANS ON THE RESISTANCE OF CHROME LEATHER TO LACTATE

Vegetable Tan	Extract offered % on drained weight	Original Leather: Cr_2O_3 g. per 100 g. (air-dry)	Original Leather: Ts °C.	After Treatment with Lactate: Cr_2O_3 g. per 100 g. (air-dry)	After Treatment with Lactate: % Cr_2O_3 extracted	After Treatment with Lactate: Ts °C.
RETANNAGE						
None	0	3.4	108	0.5	85	80
Sulfited	3	2.3	107	0.8	65	84
Quebracho	6	2.7	107	1.1	59	93
	12	2.0	105	1.1	45	98
Mimosa	3	2.4	105	0.8	66	62
	6	2.1	105	0.9	57	85
	12	1.9	106	0.8	58	88
Myrobalans	3	2.6	105	0.7	73	87
	6	2.3	102	1.3	44	92
	12	2.1	98	1.5	29	98
PRETANNAGE						
None	0	4.6	110	0.7	85	62
Sulfited	3	2.2	101	0.8	64	81
Quebracho	6	2.4	99	1.0	58	94
	12	2.3	102	1.1	52	102
Mimosa	3	2.7	101	0.8	70	85
	6	2.8	103	1.1	61	96
	12	2.2	101	1.1	50	103
Myrobalans	3	2.1	97	.8	62	85
	6	3.1	105	1.3	58	105
	12	2.6	101	1.6	38	106

On extraction with sodium lactate solutions the results were qualitatively similar to those of the first series. The vegetable tans were again the only substances which caused any appreciable reduction in the amounts of chrome extracted or in the fall in shrinkage temperature. The improved resistance observed with the resorcinol-formaldehyde resin of low molecular weight (H) was not confirmed. The naphthalene-sulfone-tanned leather had a higher chrome content and shrinkage temperature after lactate extraction than the control, but this was probably due to its higher chrome content initially rather than to any specific effect of the substance itself. Further experiments were, therefore, confined to vegetable tans.

The results obtained on retannage and pretannage with varying amounts of mimosa, sulfited quebracho, and myrobalans are shown in Table III. Retannage again caused a progressive decrease in chrome content and shrinkage temperature, but on subsequent extraction with lactate the amounts of chrome removed and the falls in shrinkage temperature decreased progressively with the extent of retannage.

In this experiment the pretannage reduced the uptake of chrome by nearly 50%. However, the presence of vegetable tan so decreased the amounts of chrome extracted by lactate that the final chrome contents and shrinkage temperatures after extraction were all greater than that of the control. The resistance to lactate increased with tan offered in the same way as with retannage.

With respect to the amounts of vegetable extract offered, pretannage gave a slightly more resistant leather than retannage, particularly with respect to hydrothermal stability. There was little choice among the three tanning materials. Perhaps rather surprisingly, myrobalans gave, if anything, the most resistant leather in both series.

The results of further experiment on retannage with myrobalans are shown in Table IV. Again the resistance to lactate increased with the amount of extract offered, and an optimum appears to be approached with about 24% of extract on drained weight. Analysis shows that at this level the ratio of vegetable tan to chrome tan (Cr_2O_3) in the leather is approximately 4 to 1.

TABLE IV

RETANNAGE OF CHROME-TANNED SHEEPSKIN WITH MYROBALANS

Extract offered on drained weight %	Leather after Tannage: Water Solubles (g. per 100 g. air-dry leather)	Leather after Tannage: Fixed Tan (g. per 100 g. air-dry leather)	Leather after Tannage: Cr_2O_3 (g. per 100 g. air-dry leather)	Ts °C.	Leather after Lactate Extraction: Cr_2O_3 g. per 100 g. air-dry leather	Leather after Lactate Extraction: Cr_2O_3 extracted, %	Leather after Lactate Extraction: Ts °C.
0	—	—	2.41	103	—	—	—
6	3.8	4.1	2.25	103	0.75	65	82
12	3.3	6.5	2.04	101	1.00	50	87
24	5.0	8.4	1.97	93	1.38	30	93
36	4.5	12.6	1.69	91	1.28	25	91

The effect of retannage of a commercial chrome split hide with mimosa and sulfited quebracho is shown in Table V. The amounts of chrome extract and the falls in shrinkage temperature resulting from extraction with lactate

TABLE V

RETANNAGE OF COMMERCIAL SPLIT HIDE WITH MIMOSA AND SULFITED QUEBRACHO

Extract offered on drained chrome leather %	Leather after Retannage			Leather after Lactate Extraction		
	Fixed Tan	Cr_2O_3	Ts	Cr_2O_3	Cr_2O_3	Ts
	g. per 100 g. air-dry leather		°C.	g. per 100 g. extracted air-dry leather, %		°C.
MIMOSA						
0	—	6.49	120	1.29	80	95
6	2.4	5.38	120	1.44	73	92
12	2.1	5.32	122	1.42	73	92
24	8.4	5.02	121	1.86	64	95
36	11.3	5.21	120	2.06	60	98
SULFITED QUEBRACHO						
6	1.2	5.14	119	1.37	73	92
12	3.0	5.28	120	1.41	73	94
24	6.8	5.07	119	1.58	69	99
36	9.6	4.99	120	1.85	63	105

decrease progressively with the amounts of tan offered, and there is little indication that an optimum has been reached. Presumably this is due to the higher chrome content; even with the highest amount offered, the ratio of fixed tan to chrome in the retanned leather only approaches 2:1.

DISCUSSION

Of the substances tested, only the vegetable tans caused any appreciable improvement in the resistance of leathers to the stripping action of a synthetic perspiration containing lactate. The amounts of chrome extracted and more particularly the falls in shrinkage temperature during treatment in such solutions were appreciably less than that of a corresponding chrome leather.

Judging from their ability to extract chrome, the other compounds were able to complex with chrome as well as react with the protein. They were, however, apparently unable to act bifunctionally and so help to "anchor" the chrome complex in the skin. Presumably the vegetable tannins, by reason of their large molecular size and ability to form a large number of hydrogen bonds with the protein, are able to serve as such an anchor.

Both pretannage and retannage were effective in improving resistance to lactate, both with respect to the amount of chrome extracted and fall in shrinkage temperature. The latter is probably the more important factor since decreased extraction of chrome may only reflect insolubility of any vegetable tan–chrome complex formed. Evidence indicates that chrome leathers only begin to deteriorate seriously under the action of moist heat when the chrome content falls to low levels, say below 2.0%, and the shrinkage temperature is reduced below 70°C. (5). High initial chrome contents are, therefore, one of the most important factors in determining initial perspiration resistance, and the fact that vegetable retannage itself removes a considerable amount of chrome and lowers the shrinkage temperature in the first place partially nullifies its purpose as a protective treatment. Pretannage has the advantage that higher initial chrome contents and shrinkage temperatures can more readily be obtained and further distribution throughout the thickness of the leather is more uniform.

There appears to be little difference among the three vegetable tanning materials tested. Although myrobalans tended to give the greatest resistance, other factors, such as its acidity, probably make this material unsuitable, at least for retannage.

In the present experiments resistance to the detanning action of lactate increased with the amount of tan offered, generally approaching the optimum with about 12% extract on drained weight. Analysis indicates that this corresponds to about 4 g. tan per g. Cr_2O_3 in the leather.

With leathers of high chrome content, relatively large amounts of tan are required to give the optimum protective action, and retannage of such leathers to increase resistance to perspiration is probably of little practical advantage, since the high chrome content is itself sufficient protection. In all these experiments the leathers were extracted with lactate only a few weeks after tannage. Further complex formation may occur during storage, and the optimum protective action may then be obtained with lower ratios of vegetable tan to chrome.

Since vegetable tan can extract chrome from leather and there is evidence that displacement of chrome from combination with protein carboxyl groups can occur during warm moist storage (1), there is presumably a maximum amount of vegetable tan in relation to chrome for optimum stability. If this is exceeded, the detannage which occurs will begin to outweigh the advantages of the increased stability conferred on the remaining chrome. This might be expected to occur when the amount of vegetable tan exceeds a 1:1 molar ratio to the number of unipointly fixed chrome complexes. On the basis of two chrome atoms per complex and an average molecular weight for the tannin components of 1500, the value of 4 g. tan per g. Cr_2O_3, which appears to give optimum resistance to lactate, corresponds to only half a mole of tan per chrome complex.

Chrome leathers containing even small amounts of vegetable tan have been found to deteriorate extensively when stored over water at 40°C. for six months (1); nevertheless, it is generally found that in wear the combination leathers are superior to either full chrome or vegetable-tanned leathers. The present findings offer a partial explanation of these observations; presumably the greater resistance of the combination-tanned leathers to perspiration outweighs their poor resistance to moist heat alone.

Further information on the resistance of vegetable-chrome combination leathers to the combined action of perspiration and moist heat and on the interaction of vegetable tan with chrome is required. These items are considered in further papers in this series.

REFERENCES

1. Bowes, J. H., and Raistrick, A. S. *JALCA*, **56**, 606 (1961).
2. Raistrick, A. S. *JALCA*, **56**, 616 (1961).
3. Bowes, J. H., and Raistrick, A. S. *JALCA*, **56**, 632 (1961).
4. ——— and Moss, J. A. *J. Soc. Leather Trades Chemists*, **44**, 419 (1960).
5. ——— and Raistrick, A. S. In preparation.
6. Gustavson, K. H. *Chemistry of the Tanning Processes* (New York: Academic Press, 1956) p. 122.
7. ———. *JALCA*, **50**, 414 (1955).
8. *Official Methods of Analysis*. Soc. Leather Trades Chemists, 1951, p. 104.
9. *Official Methods of Analysis*. Soc. Leather Trades Chemists, 1951.
10. *JALCA*, **40**, 7 (1945).