# THEORETICAL ASPECTS OF THE REACTION OF ZIRCONIUM COMPOUNDS AND VEGETABLE TANNINS WITH THE CHROMIUM-COLLAGEN COMPLEX.


by

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## VOLUME 2

All of the technological work described in Volume 1 has been taken from the author's Research Bulletins published by the Leather Industries Research Institute, the most important of which are reproduced in this Volume. Thus details of experimental procedure and complete results of technological importance are available for reference.

The work is divided into two parts : in the first part, the Bulletins dealing with the reaction of zirconium with chromium tanned pelt are presented, and in the second a selection of the Bulletins dealing with the retannage of chromium tanned leather with vegetable tannins is given.

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# PART I

## RETANNAGE OF CHROMIUM TANNED LEATHER WITH ZIRCONIUM COMPOUNDS

# R.B. 315. CHROMIUM/ZIRCONIUM COMBINATION TANNAGES

by

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## SUMMARY

An investigation has been made of a current commercial process for the manufacture of chromium/zirconium combination tanned leather. Factors that were thought to be important in determining the quality of the leather are the amount of chrome, the use of a chrome stable oil, the use of a strong complexing agent, the amount of zirconium offered as a retannage, the addition of oil during the zirconium tannage, and a syntan topping.

The leather had excellent physical properties and none of the variables had serious effects on the characteristics measured. The higher chrome content gave softer leather but the strength characteristics were lower. The sulphited oil increased the fixation of the chrome and resulted in a higher shrinkage temperature, increased softness, but yielded a slightly looser if more extensible grain. Citric acid increased the fixation of zirconium, slightly increased the shrinkage temperature and produced softer leather with a looser grain; strength and lastometer extension were improved. The higher zirconium content reduced the pH of the leather which had a slightly lower shrinkage temperature and impaired strength and stretch. The presence of oil in the zirconium liquor had little effect on the physical properties but there was a trend in favour of a cationic oil; the emulsified oils had no beneficial effect. A syntan topping improved the appearance of the leather.

## INTRODUCTION

Although zirconium is a mineral tanning material, the mechanism of its reaction with pelt is generally considered to be similar to that of vegetable tannins since it gives plump firm leather [(1)]. Since the character of the leather produced by zirconium tannage is very much like that of vegetable tanned leather, use is made of zirconium for retanning chrome tanned stock [(2)]. This procedure produces leather which has several advantages over the conventional chrome-retan leather. Chief among these are the absence of materials which interact to produce acid or tender leather, an all-mineral tannage with better dyeing properties, and very pale coloured leather which forms an excellent base for pastel shades.

Numerous disadvantages are to be recognised, the most important of which is the cost of the zirconium tanning materials. Other drawbacks are the difficulty in obtaining zirconium penetration, the difficulty in obtaining fatliquor penetration and the need to reduce the harsh feel of the leather.

Suitable formulations have been worked out by the suppliers of various raw materials but no comprehensive study of the various factors has been made. In practice the procedure which has been found to be most satisfactory consists of the following [2].

The chrome tanned pelt after shaving is adjusted to a pH of 3 or below with sulphuric acid, then citric acid is added, followed by the dry zirconium salt. In view of the dry nature of the tannage a cationic oil is added during the tannage and this helps the skins to tumble in the drum without an excessive build-up of heat. Drumming is continued for several hours until the zirconium is taken up. The goods are neutralised, then topped with a suitable syntan. As in the case of conventional chrome-vegetable leather, slightly more fatliquor is needed than for full-chrome leather, and in order to ensure that the emulsion does not break on the surface, a small amount of non-ionic surface active agent may have to be incorporated.

This experiment was undertaken to investigate the zirconium retannage of chrome leather and to explore the effects of the various recommended factors on the physical properties of the leather. Specimens have also been subjected to the accelerated ageing test and to natural ageing for nine months, but the results of the ageing are reported separately.

## EXPERIMENTAL

### Plan of the Experiment

The experiment was planned as a $\frac{1}{4}$ replicate of a $2^9$ factorial design, giving a total of 128 treatment combinations. The factors varied and the levels of the factors were as follows:

A Amount of chrome offered.

(1) 0.5% $Cr_2O_3$ as 33% basic chrome salt
a 2.0% $Cr_2O_3$ as 33% basic chrome salt

B Chrome stable fatliquor used in the chrome tannage.

(1) None
b 1% sulphited chrome stable fatliquor

C Pre-retan additions.

- (1) None
- c 1% citric acid

D Amount of zirconium tanning salt offered.

- (1) 1.25% $ZrO_2$ as 45% basic salt
- d 2.0% $ZrO_2$ as 45% basic salt

EF Addition of oil during zirconium tannage.

- (1) None
- e 1% cationic fatliquor
- f ½% cationic fatliquor + ½% raw neatsfoot oil
- ef 1% raw neatsfoot oil + 5% non-ionic surface active agent on oil weight

GH Addition of syntan after zirconium tannage.

- (1) None
- g 1% neutralised syntan
- h 1% replacement type white syntan
- gh 1% complex basic aluminium salt

J Neutralising Material.

- (1) 2% sodium bicarbonate
- j 1% sodium acetate + 1% sodium bicarbonate

Process Details

Eight limed calfskins were each cut into 16 samples, giving a total of 128 specimens.

The samples were delimed with 1% boric acid in a float of 100% water at 35°C for 30 minutes, then 1% Pancreol 3A was added to the float, for 30 minutes. After sorting for factors A and B the samples were pickled for one hour in a 100% float containing 5% salt and 0.5% sulphuric acid. The (1) and "a" samples were tanned with 0.5% and 2% $Cr_2O_3$ respectively. The "b" and "ab" samples also received 0.5% and 2% $Cr_2O_3$ respectively plus 1% of sulphited chrome stable fatliquor. Tannage was effected by adding one-third of the chrome liquor and one-half of the fatliquor alternately at 20 minute intervals. After the last addition the samples were drummed for four hours, left in the liquor over-night and were drummed for a further hour the following morning, during which time the pH was adjusted to 3.7 where necessary.

The samples were sorted for factors C, D and EF. Each group of samples was placed in 50% water and the pH was adjusted to below 3 with sulphuric acid. All "c" samples received 1% citric acid while drumming continued for 10 minutes. Then the requisite quantity of dry zirconium tanning salt was added to each group which was then drummed for 10 minutes, and finally the oil as specified by factor EF was added. Drumming was continued for two hours, when the pH was slowly raised to 4.5 with sodium bicarbonate. The samples were piled over-night, then sorted for factor GH and retanned with syntan in a 100% float for 30 minutes. The leathers were washed, then sorted for factor J, and neutralised. They were washed with cold water, then warmed to 50°C, and fatliquored with an emulsion of 1% raw neatsfoot oil and 3% sulphated neatsfoot oil containing 2% titanium dioxide, at 50°C for 40 minutes. The samples were horsed over-night, then tacked out to dry, damped back, staked, redried, and plated at 150°F and 1800 lb./in.$^2$ pressure.

The samples were assessed for stiffness, looseness of the grain, and colour. Triplicate samples were cut for lastometer load and extension at grain crack and slit tear strength. One set of samples was for immediate testing, another set for testing after three weeks accelerated ageing at 48°C and 95+% r.h., while the third set was for testing after nine months natural ageing. The pH values of the samples were determined on the unaged and on the aged samples and composite samples of various factors were made up for the determination of chrome, zirconium and aluminium content.

The extractable fats and oils content was determined on the lastometer samples by extraction in a Davies extractor. The shrinkage temperature was determined on the unaged leathers.

All samples were conditioned at 20°C and 65% r.h. before testing, and results reported were significant at the 5% level.

## RESULTS

### ANALYTICAL

#### pH Determinations

Leathers tanned with 0.5% $Cr_2O_3$ were found to have a higher pH value than those tanned with 2% $Cr_2O_3$. Neutralisation with 2% sodium bicarbonate gave a higher pH value than neutralisation with a mixture of 1% sodium bicarbonate and 1% sodium acetate, but the difference in pH for the two types of neutralisation was greater at the 2% level of $Cr_2O_3$. This interaction is given in Table I.

Table I
pH Values

| Neutralisation | Amount of Chrome | | Mean |
|---|---|---|---|
| | 0,5% $Cr_2O_3$ | 2% $Cr_2O_3$ | |
| 2% $NaHCO_3$ | 4.45 | 4.38 | 4.41 |
| 1% $NaHCO_3$ + 1% Na acetate | 4.33 | 4.12 | 4.22 |
| Mean | 4.39 | 4.25 | 4.32 |

At the low level of zirconium tannage the addition of citric acid before retannage lowered the pH of the leather, whereas at the high level of zirconium the addition of citric acid made little difference to the pH values. The pH of the leather was found to be lower for the high level of zirconium retannage. This interaction is given in Table II.

Table II
pH Values

| Amount of Retanning material | Pre-retan Additions | | Mean |
|---|---|---|---|
| | none | citric acid | |
| 4% zirconium tanning salt | 4.41 | 4.31 | 4.36 |
| 7% zirconium tanning salt | 4.25 | 4.30 | 4.28 |
| Mean | 4.33 | 4.31 | 4.32 |

Addition of oil during retannage raised the pH of the leather slightly. This effect was more apparent at the low level of zirconium tannage, as can be seen from Table III.

Table III
pH Values

| Amount of Retanning material | Addition of Oil | | | | Mean |
|---|---|---|---|---|---|
| | none | 1% cationic fatliquor | 0,5% cationic fatliquor + 0,5% raw neatsfoot | 1% raw neats-foot | |
| 4% zirconium tanning salt | 4.25 | 4.40 | 4.35 | 4.43 | 4.36 |
| 7% zirconium tanning salt | 4.28 | 4.24 | 4.31 | 4.27 | 4.28 |
| Mean | 4.26 | 4.32 | 4.33 | 4.35 | 4.32 |

Addition of syntan resulted in an increase in the pH value of the leather at the low level of chrome tannage, but at the high level of chrome the addition of syntan did not appreciably change the pH values. This result is given in Table IV.

Table IV
pH Values

| Amount of Chrome | Addition of Syntan | | | | Mean |
|---|---|---|---|---|---|
| | none | neutralised syntan | replacement type white syntan | complex basic Al salt | |
| 0.5% $Cr_2O_3$ | 4.33 | 4.44 | 4.38 | 4.38 | 4.38 |
| 2.0% $Cr_2O_3$ | 4.27 | 4.23 | 4.19 | 4.31 | 4.23 |
| Mean | 4.30 | 4.33 | 4.28 | 4.34 | 4.31 |

Chromium Content

At the low level of chrome tannage the addition of a chrome stable fatliquor considerably increased the chrome uptake, whereas at the high level of chrome the fatliquor did not affect the chrome uptake. This interaction is given in Table V.

Table V
Chrome Content, % $Cr_2O_3$

| Addition of Chrome Stable Fatliquor | Amount of Chrome | | Mean |
|---|---|---|---|
| | 0.5% $Cr_2O_3$ | 2.0% $Cr_2O_3$ | |
| none | 1.19 | 3.18 | 2.19 |
| sulphited oil | 2.22 | 3.08 | 2.65 |
| Mean | 1.70 | 3.13 | 4.42 |

Zirconium Content

At the 4% level of zirconium retannage the addition of citric acid prior to retannage resulted in a slightly higher zirconium uptake. At the 7% level of zirconium retannage the citric acid did not affect the zirconium uptake. These values are given in Table VI.

Table VI
Zirconium Content, % $ZrO_2$

| Pre-retan additions | Amount of Retanning Material | | |
|---|---|---|---|
| | 4% zirconium tanning salt | 7% zirconium tanning salt | Mean |
| none | 1,67 | 3,47 | 2,57 |
| citric acid | 1,93 | 3,45 | 2,69 |
| Mean | 1,80 | 3,46 | 2,63 |

## Aluminium Content

1% complex basic aluminium salt on the blue weight of the leather resulted in an aluminium content of 0,26% $Al_2O_3$.

## Extractable Fats and Oils

The extractable fats and oils content was increased by the addition of a chrome stable fatliquor during chrome tannage. This effect was more pronounced at the 0,5% level of $Cr_2O_3$ than at the 2% level of $Cr_2O_3$. This interaction is given in Table VII.

Table VII
Extractable Fats and Oils, %

| Chrome Stable fatliquor | Amount of Chrome | | |
|---|---|---|---|
| | 0,5% $Cr_2O_3$ | 2,0% $Cr_2O_3$ | Mean |
| none | 5,54 | 5,86 | 5.70 |
| sulphited oil | 7.57 | 6.57 | 7.07 |
| Mean | 6,55 | 6,22 | 6.39 |

At the 0,5% level of $Cr_2O_3$, retanning with 4% zirconium tanning salt resulted in a slightly higher extractable fats and oils content of the leather than retannage with 7% zirconium tanning salt. At the 2,0% level of $Cr_2O_3$ the amount of retanning material did not appreciably affect the amount of extractable fats and oils. These results are given in Table VIII.

Table VIII
Extractable Fats and Oils, %

| Amount of Retanning Material | Amount of Chrome $0.5\%$ $Cr_2O_3$ | $2.0\%$ $Cr_2O_3$ | Mean |
|---|---|---|---|
| 4% zirconium tanning salt | 6.95 | 6.15 | 6.55 |
| 7% zirconium tanning salt | 6.17 | 6.27 | 6.22 |
| Mean | 6.56 | 6.21 | 6.39 |

The type of syntan offered to the leather affected the extractable fats and oils content of the leather as follows: no syntan, 6.34%; 1% neutralised syntan, 5.67%; 1% replacement type white syntan, 6.87%; 1% complex basic aluminium salt, 6.66%.

Shrinkage Temperature

As was to be expected, the shrinkage temperature of the leathers was higher at the 2% level of chrome than at the 0.5% level of chrome. However, at the 0.5% level of $Cr_2O_3$ the addition of a chrome stable fatliquor during chrome tannage increased the shrinkage temperature of the leather considerably, whereas at the 2% level of $Cr_2O_3$ the shrinkage temperature was unaffected by the application of the sulphited oil. This interaction is given in Table IX.

Table IX
Shrinkage Temperature

| Chrome stable fatliquor | Amount of Chrome $0.5\%$ $Cr_2O_3$ | $2.0\%$ $Cr_2O_3$ | Mean |
|---|---|---|---|
| none | 89.8 | 101.4 | 95.6 |
| sulphited chrome-stable fatliquor | 96.4 | 100.9 | 98.7 |
| Mean | 93.1 | 101.2 | 97.2 |

The shrinkage temperature was lower at the 7% level of zirconium tannage than at the 4% level of zirconium, but when 1% citric acid was added to the float before retanning, the level of retannage had no effect on the shrinkage temperature. In general, addition of citric acid raised the shrinkage temperature of the leather. This interaction is given in Table X.

Table X
Shrinkage Temperature

| Amount of Retanning Material | Pre-retan addition | | Mean |
|---|---|---|---|
| | none | citric acid | |
| 4% zirconium tanning salt | 97.4 | 98.1 | 97.8 |
| 7% zirconium tanning salt | 94.7 | 98.3 | 96,5 |
| Mean | 96.1 | 98.2 | 97.2 |

At the 4% level of zirconium the shrinkage temperature was raised slightly by the addition of oil during retannage, whereas at the 7% level of zirconium the addition of oil did not have an appreciable effect on the shrinkage temperature. This result is given in Table XI.

Table XI
Shrinkage Temperature

| Amount of Retanning Material | Addition of oil | | | | Mean |
|---|---|---|---|---|---|
| | none | 1% cationic fatliquor | ½% cationic fatliquor + ½% raw neatsfoot | 1% raw neatsfoot | |
| 4% zirconium tanning salt | 96.9 | 99.2 | 97.1 | 98.3 | 97.9 |
| 7% zirconium tanning salt | 96.6 | 96.1 | 97.4 | 95.6 | 96.4 |
| Mean | 96.8 | 97.7 | 97.3 | 97.0 | 97.2 |

Addition of citric acid prior to retannage resulted in a higher shrinkage temperature irrespective of the type of syntan offered after retannage. In general, the application of syntan had little effect on the shrinkage temperature. This result is given in Table XII.

Table XII
Shrinkage Temperature

| Pre-retan addition | Addition of Syntan: none | Addition of Syntan: neutralised syntan | Addition of Syntan: replacement type white syntan | Addition of Syntan: complex basic Al salt | Mean |
|---|---|---|---|---|---|
| none | 96.2 | 96.7 | 95.6 | 95.8 | 96.1 |
| citric acid | 97.3 | 96.8 | 99.4 | 99.4 | 98.1 |
| Mean | 96.8 | 96.8 | 97.5 | 97.6 | 97.1 |

## PHYSICAL PROPERTIES

### Stiffness

The stiffness was determined manually. The leathers were sorted into six groups according to their flexibility and scored as follows: 0, very flexible, 5, very firm.

The leathers were found to be firmer at the 0.5% level of $Cr_2O_3$ than at the 2.0% level of $Cr_2O_3$, and the flexibility of the leathers was increased by the addition of a chrome stable fatliquor during chrome tannage especially at the 0.5% $Cr_2O_3$ level. This interaction is given in Table XIII.

Table XIII
Stiffness

| Chrome stable fatliquor | Amount of Chrome: 0.5% $Cr_2O_3$ | Amount of Chrome: 2.0% $Cr_2O_3$ | Mean |
|---|---|---|---|
| none | 3.5 | 2.4 | 2.95 |
| sulphited oil | 2.6 | 2.6 | 2.60 |
| Mean | 3.05 | 2.50 | 2.78 |

The leathers were found to be firmer when neutralised with 2% sodium bicarbonate (score 2.93) than with a mixture of 1% sodium bicarbonate and 1% sodium acetate (score 2.68).

Colour

The leathers were sorted into five groups according to their depth of colour which was assessed visually. The scoring was on the basis of 0, almost white; 4, fairly blue.

The samples tanned with 2% $Cr_2O_3$ were much bluer in colour than those tanned with only 0.5% $Cr_2O_3$. Retannage with 7% zirconium tanning salt reduced the blueness of the leather slightly at the 0.5% level of chrome. These results are given in Table XIV.

Table XIV
Colour

| Amount of Retanning material | Amount of Chrome | | Mean |
|---|---|---|---|
| | 0.5% $Cr_2O_3$ | 2.0% $Cr_2O_3$ | |
| 4% zirconium tanning salt | 1.4 | 2.8 | 2.1 |
| 7% zirconium tanning salt | 1.0 | 3.0 | 2.0 |
| Mean | 1.2 | 2.9 | 2.1 |

Addition of oil during zirconium tannage resulted in slightly bluer leather. This effect became more pronounced when citric acid was added before retannage except when raw neatsfoot oil was used. This interaction is given in Table XV.

Table XV
Colour

| Pre-retan additions | Addition of Oil | | | | Mean |
|---|---|---|---|---|---|
| | none | 1% cationic fatliquor | ½% cationic fatliquor + ½% raw neatsfoot | 1% raw neatsfoot | |
| none | 1.8 | 2.1 | 1.6 | 2.3 | 1.9 |
| citric acid | 1.9 | 2.6 | 2.4 | 1.7 | 2.2 |
| Mean | 1.8 | 2.4 | 2.0 | 2.0 | 2.1 |

Treatment with chrome stable fatliquor during chrome tannage resulted in slightly whiter leather : no fatliquor, 2.2; 1% sulphited chrome stable fatliquor, 1.9.

Treatment with neutralised syntan gave slightly whiter leather than any of the other syntan treatments; no syntan, 2.3; neutralised syntan, 1.7; replacement type white syntan, 2.3; complex basic aluminium salt, 2.0.

Looseness of the Grain

This property was assessed visually. The leathers were sorted into four groups according to the looseness of the grain, and scored as follows: 0, fine grain; 3, loose grain.

It was found that addition of chrome stable fatliquor resulted in slightly looser grain in all cases except where the leather was offered neutralised syntan when this trend was reversed. The average figures are: no fatliquor, 1.33; 1% sulphited chrome stable fatliquor, 1.40.

The grain tended to be looser when the samples were tanned with 2.0% $Cr_2O_3$ instead of 0.5% $Cr_2O_3$. This difference was greater in the case where no fatliquor had been added during chrome tannage. This result is given in Table XVI.

Table XVI
Looseness of the Grain

| Chrome stable fatliquor | Amount of Chrome | | Mean |
|---|---|---|---|
| | 0.5% $Cr_2O_3$ | 2.0% $Cr_2O_3$ | |
| none | 1.00 | 1.66 | 1.33 |
| sulphited oil | 1.34 | 1.47 | 1.46 |
| Mean | 1.17 | 1.57 | 1.37 |

Addition of citric acid prior to retannage resulted in leather with looser grain than that which had received no citric acid. The results are: no citric acid, 1.19; 1% citric acid, 1.55.

Thickness

Owing to the accuracy with which the thickness could be determined, small differences in thickness were found to be highly significant, although they may not be of economic importance.

The leather tended to be thicker when tanned with the low level of chrome : 0.5% $Cr_2O_3$, 0.79 mm.; 2.0% $Cr_2O_3$, 0.73 mm.

The addition of a chrome stable fatliquor during chrome tannage resulted in thicker leather : no fatliquor, 0.74 mm.; 1% sulphited chrome stable fatliquor, 0.78 mm.

In general, the addition of citric acid prior to zirconium retannage produced thinner leather if the leather was subsequently treated with syntan. In the case where no syntan or complex basic aluminium salt was offered there was no difference in the thickness. This interaction is given in Table XVII.

Table XVII
Thickness, mm.

| Pre-retan additions | Addition of Syntan | | | | Mean |
|---|---|---|---|---|---|
| | none | neutralised syntan | replacement type white syntan | complex basic Al salt | |
| none | 0.77 | 0.80 | 0.84 | 0.73 | 0.79 |
| citric acid | 0.75 | 0.74 | 0.70 | 0.75 | 0.74 |
| Mean | 0.76 | 0.77 | 0.77 | 0.74 | 0.76 |

Lastometer Load at Grain Crack

Tannage with 2.0% $Cr_2O_3$ resulted in stronger leather than tannage with 0.5% $Cr_2O_3$, but when citric acid was added before retannage stronger leather was obtained at the low level of chrome. This interaction is given in Table XVIII.

Table XVIII
Lastometer Load at Grain Crack, lb./in.

| Pre-retan additions | Amount of Chrome | | Mean |
|---|---|---|---|
| | 0.5% $Cr_2O_3$ | 2.0% $Cr_2O_3$ | |
| none | 2675 | 2916 | 2796 |
| citric acid | 3116 | 2794 | 2955 |
| Mean | 2896 | 2855 | 2876 |

The grain strength of the leather was better at the low level of zirconium retannage than at the high level of retannage but this is a result of the addition of chrome stable fatliquor at this level. At the high level of zirconium retannage, the chrome stable fatliquor had no effect. This interaction is given in Table XIX

Table XIX

Lastometer Load at Grain Crack, lb./in.

| Amount of Retanning Material | Chrome Stable Fatliquor | | Mean |
|---|---|---|---|
| | none | sulphited oil | |
| 4% zirconium tanning salt | 2900 | 3353 | 3127 |
| 7% zirconium tanning salt | 2656 | 2591 | 2623 |
| Mean | 2778 | 2972 | 2875 |

It was found that neutralisation with sodium bicarbonate only increased the grain strength by comparison with the mixed neutralising agent. Average results for the two neutralising materials are: 2% $NaHCO_3$, 2995 lb./in.; 1% $NaHCO_3$ & 1% Na acetate, 2749 lb./in.

Treatment with neutralised syntan reduced the lastometer strength of the leather, whereas the other syntans had no effect on the grain strength. This result is illustrated by the following figures: no syntan, 3004 lb./in.; neutralised syntan, 2597 lb./in.; replacement type white syntan, 2960 lb./in.; complex basic aluminium salt, 2941 lb./in.

Lastometer Extension at Grain Crack

The leather tended to be more extensible if tanned with 2.0% $Cr_2O_3$. This effect was reversed when citric acid was added before retannage. This result is shown in Table XX.

Table XX

Lastomer Extension at Grain Crack, mm.

| Pre-retan addition | Amount of Chrome | | Mean |
|---|---|---|---|
| | 0.5% $Cr_2O_3$ | 2.0% $Cr_2O_3$ | |
| none | 11.48 | 12.23 | 11.85 |
| citric acid | 12.52 | 11.90 | 12.21 |
| Mean | 12.00 | 12.06 | 12.03 |

Retannage with the low amount of zirconium resulted in more extensible leather than retannage with the high amount of zirconium. The extension at grain crack was further increased where the leather had been treated with chrome stable fatliquor during chrome tannage. This interaction is shown in Table XXI.

Table XXI

Lastometer Extension at Grain Crack, mm.

| Amount of Retanning Material | Chrome Stable Fatliquor | | Mean |
|---|---|---|---|
| | none | sulphited oil | |
| 4% zirconium tanning salt | 11.78 | 13.23 | 12.50 |
| 7% zirconium tanning salt | 11.56 | 11.57 | 11.56 |
| Mean | 11.67 | 12.40 | 12.03 |

The addition of fatliquor during chrome tannage increased the extensibility of the leather, but when citric acid was used as a pre-retan addition the extensibility was also increased and the influence of the chrome stable fatliquor was reduced. This interaction is shown in Table XXII.

Table XXII
Lastometer Extension at Grain Crack, mm.

| Pre-retan addition | Chrome Stable Fatliquor | | Mean |
|---|---|---|---|
| | none | sulphited oil | |
| none | 11.22 | 12.50 | 11.86 |
| citric acid | 12.13 | 12.29 | 12.21 |
| Mean | 11.67 | 12.39 | 12.03 |

Although the extension at grain crack was increased by the use of a chrome stable fatliquor, the same effect was achieved by the addition of a cationic fatliquor during zirconium retannage. None of the other oils offered during retannage affected the extensibility of the leather. This result is given in Table XXIII.

Table XXIII
Lastometer Extension at Grain Crack, mm.

| Chrome stable fatliquor | Addition of Oil | | | | Mean |
|---|---|---|---|---|---|
| | none | 1% cationic fatliquor | ½% cationic fatliquor + ½% raw neatsfoot | 1% raw neatsfoot | |
| none | 11.42 | 12.32 | 11.41 | 11.49 | 11.66 |
| sulphited oil | 12.71 | 12.22 | 12.62 | 12.04 | 12.40 |
| Mean | 12.06 | 12.27 | 12.01 | 11.76 | 12.03 |

The extension at grain crack of the leather was reduced by the addition of a neutralised syntan, 11.47 mm.; and increased by treatment of the leather with a replacement type white syntan, 12.49 mm.; whereas complex basic aluminium salt did not affect the extension of the leather, 12.11 mm. The average extension of those samples which had received no syntan was 12.06 mm.

Slit Tear Strength

The tearing strength of the leather was improved when only 0.5% $Cr_2O_3$ was offered for tannage. At this level of chrome tannage, retannage with 4% zirconium tanning salt gave much stronger leather than retannage with 7% zirconium. At the 2% level of $Cr_2O_3$ the amount of retanning material did not influence the strength appreciably. This interaction is given in Table XXIV.

Table XXIV
Slit Tear Strength, lb./in.

| Amount of Retanning Material | Amount of Chrome | | Mean |
|---|---|---|---|
| | 0.5% $Cr_2O_3$ | 2.0% $Cr_2O_3$ | |
| 4% zirconium tanning salt | 602.8 | 479.4 | 541.1 |
| 7% zirconium tanning salt | 493.4 | 488.1 | 490.7 |
| Mean | 548.1 | 483.7 | 515.9 |

The slit tear strength was increased by addition of citric acid prior to retannage. The following figures illustrate this result : no citric acid, 489.7 lb./in.; citric acid, 550.0 lb./in.

## DISCUSSION

The leathers prepared in this experiment possessed very good slit tear strengths and excellent lastometer loads and extensions at grain crack. The average values for these properties are: slit tear strength, 516 lb./in.; lastometer load at grain crack, 2875 lb./in. and lastometer extension at grain crack, 12.00 mm. These figures correspond to expected values for full-chrome leather and are considerably in excess of average physical properties of conventional chrome-retan leather. Since the strength characteristics depend largely on the quality of the raw skin from which the leather was prepared, only very general observations can be made regarding the relative properties of full-chrome, chrome-retan and chrome/zirconium tanned leather. Nevertheless, in view of the excellent physical properties, retannage of chrome tanned leather with zirconium would appear to have no serious drawbacks as far as quality is concerned.

Of the factors varied in this experiment none have had a very serious influence on the properties. The amount of chrome offered obviously affected the chrome content, the shrinkage temperature and the pH of the leather. Of the physical properties, increased chrome resulted in an increase in the softness of the leather, in a bluer colour of the white surface and in greater looseness of the grain. Strength characteristics were better at the low level of chrome tannage although the level of zirconium tannage also influenced this property. The lastometer extension was unaffected by this factor.

The use of a chrome stable fatliquor during the chrome tannage caused greater fixation of the chrome, and a higher shrinkage temperature, and resulted in a greater fats and oils content. Greater flexibility and slightly looser but more extensible grain was noted when the sulphited oil was used, but it had no influence on the strength or lastometer load.

The addition of citric acid increased the fixation of zirconium, slightly increased the shrinkage temperature, produced softer leather and caused slightly looser grain. The slit tear strength and lastometer load were increased when citric acid was used, and the lastometer extension was slightly greater.

The amount of zirconium offered during the retannage was important; the greater quantity of $ZrO_2$ resulting in a lower pH, slightly lower shrinkage temperatures and an increased zirconium content. The higher level of zirconium tannage resulted in lower slit tear and grain strengths, and reduced the lastometer extension at grain crack.

The addition of oil during zirconium tannage had surprisingly little effect, none of the properties being significantly influenced. There was a trend in favour of the use of a cationic oil but the use of an emulsified raw oil was not beneficial as far as physical properties are concerned. Undoubtedly the presence of oil will assist the mechanical action in the drum and prevent excessive frictional heat being generated.

The application of a syntan topping in one case reduced the uptake of fat, but in others had no influence on the extractable fats in the leather. Where syntan had been used the leathers tended to be somewhat stiffer, paler in colour and stronger but the grain strength was lower. The use of one of the syntans materially reduced the extension at grain crack.

In general, the process currently in commercial use appears to be the optimum as far as variations of individual steps are concerned, and the leather has a good feel and excellent physical properties.

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# R.B. 342. AGEING CHARACTERISTICS OF CHROMIUM/ZIRCONIUM COMBINATION TANNAGES

by

D.A. Williams-Wynn and U. Jaeger.

## SUMMARY

An investigation has been made of the storage stability of chromium/zirconium combination tanned leather. Various factors in the manufacture of the leathers were thought to be important. These included the amount of chromium, the use of chrome-stable oil, the use of a strong complexing agent, the amount of zirconium offered as a retannage, the addition of oil during the zirconium tannage, and a syntan topping.

The leather had excellent physical properties and wasstable under both normal and high temperature and humidity conditions of storage. The grain showed signs of becoming tender, but even after prolonged ageing the grain characteristics were good.

Increasing the degree of both chrome and zirconium tanning resulted in more durable leather, and the application of complexing and buffering compounds during the processing also resulted in an improvement in storage stability. Only certain of the oils added during the tannages were beneficial. The application of a sulphited oil during chrome tanning and a non-ionic emulsified oil during zirconium tanning were advantageous, but a cationic oil imparted no improved stability on storage.

Combination tannages involving chromium and zirconium give good quality strong leather with reasonable resistance to ageing even under the most rigorous conditions.

## INTRODUCTION

Zirconium is frequently used for retanning chrome tanned stock in order to improve its fullness and plumpness and in particular to tighten the grain. Thus it is used for the same purpose that synthetic and vegetable tanning agents are used. It has been shown that, although zirconium is a mineral tanning agent, the mechanism of its reaction with pelt is similar to that of vegetable tannins [(1)]. However, it is not likely to cause deterioration in the same way that vegetable tannins do and in fact no evidence is to be found in the literature that deterioration of chrome/zirconium leather occurs. Nevertheless it is important to determine to what extent leathers of this kind do deteriorate on storage.

In a previous report (see preceeding section) results were given of the effect of various factors in the manufacture of combination tanned leather on the properties of the leather [2]. Samples of these leathers were retained for ageing tests under both natural conditions of storage, and the conditions of the accelerated ageing test developed for chrome-retan leathers [3, 4]. The results of these ageing trials are given in this report.

Details of the factors varied and of the preparation of the leathers are given above.

## RESULTS OF AGEING

### Difference in Slit Tear Strength on Accelerated Ageing

On average the leathers lost no strength after the accelerated ageing test. Some leathers lost strength whilst others gained slightly in strength but the only factor that significantly influenced the difference from the original was the level of chrome tannage, the higher chrome content resulting in stronger leather. The average values for the two levels of chrome tannage are: 0.5% $Cr_2O_3$ lost 21.7 lb./in. (4.4%) whereas 2.0% $Cr_2O_3$ gained 22.0 lb./in. (4.5%).

No other factor materially affected the change in strength on accelerated ageing.

### Difference in Slit Tear Strength on Natural Ageing

The leathers were aged in the standard atmosphere, 20°C and 65% r.h., for one year before testing. The average loss of strength on ageing was 56.3 lb./in. (10.2%) and the factor that had the most significant influence on this property was the level of chrome tannage. The average values for the two levels are: 0.5% $Cr_2O_3$ lost 82.3 lb./in. (16%) and 2.0% $Cr_2O_3$ lost 20.6 lb./in. (4%).

The type of neutralising material used influenced the deterioration on natural ageing, the presence of buffer salt resulting in less loss of strength. The average losses for the two neutralising agents are : 2% sodium bicarbonate, 81.9 lb./in. (16%) and 1% sodium acetate plus 1% sodium bicarbonate, 21.1 lb./in. (4%).

Differences in Lastometer Load at Grain Crack on Accelerated Ageing

The deterioration in grain strength was reduced by incorporating citric acid prior to retannage with zirconium, particularly in the case where a chrome stable fatliquor had been used during the chrome tannage. This interaction is given in Table I.

Table I
Loss of Lastometer Load on Accelerated Ageing, lb./in.

| Pre-retan additions | Chrome-stable Fatliquor | | Mean |
|---|---|---|---|
| | none | sulphited oil | |
| none | 612 | 653 | 632 |
| citric acid | 575 | 178 | 377 |
| Mean | 593 | 416 | 504 |

The percentage losses of strength for the leathers containing citric acid and without citric acid are 12.7% and 22.5% respectively.

The loss of grain strength was less when the larger quantity of zirconium was used for retanning, the average values for the two levels of retannage being: 4% zirconium retanning salt lost 664 lb./in. (23%) and 7% zirconium retanning salt lost 345 lb./in. (12%). These results are however dependent on the use of syntan topping, the two syntans causing less deterioration than either the complex aluminium salt or the absence of any after-treatment. The average results for the four after treatments are: no syntan topping lost 641 lb./in. (22%), 1% neutral syntan lost 312 lb./in. (11%), 1% replacement white syntan lost 450 lb./in. (16%) and the complex aluminium salt lost 615 lb./in. (21%). The interaction of these two factors is given in Table II.

Table II
Fall in Lastometer Load on Accelerated Ageing, lb./in.

| | Addition of Syntan Topping | | | | Mean |
|---|---|---|---|---|---|
| | none | neutral syntan | replacement syntan | complex aluminium | |
| 4% zirconium | 719 | 431 | 713 | 794 | 664 |
| 7% zirconium | 563 | 194 | 187 | 437 | 345 |
| Mean | 641 | 312 | 450 | 615 | 504 |

The application of a non-ionic oil emulsion during the zirconium retannage resulted in less deterioration than when oils were absent or cationic oils were used. The average values for the four groups of leather are: no oil added lost 525 lb./in. (18%); 1% cationic fatliquor lost 537 lb./in. (19%); 0.5% cationic fat plus 0.5% raw neatsfoot oil lost 590 lb./in. (20%); non-ionic emulsified neatsfoot oil lost 366 lb./in. (13%).

Differences in Lastometer Load at Grain Crack on Natural Ageing

The average loss of grain strength on natural ageing was 332 lb./in. (11.5%), compared with 504 lb./in. (17.5%) loss on accelerated ageing.

The application of citric acid before zirconium retannage resulted in less deterioration on storage, the average losses being: no citric acid 431 lb./in. (15%), and 1% citric acid 232 lb./in. (8%). The application of a chrome stable fatliquor during the chrome tannage also resulted in less deterioration, the average fall in strength for each group being: no sulphited oil 435 lb./in. (15%) and 1% sulphited oil 239 lb./in. (8%), but these values are dependent on the presence of citric acid. This interaction is given in Table III.

Table III

Fall in Lastometer Load on Natural Ageing. (lb./in.)

| Pre-retan additions | Chrome-stable Fatliquor | | Mean |
|---|---|---|---|
| | none | sulphited oil | |
| none | 485 | 378 | 431 |
| citric acid | 385 | 79 | 232 |
| Mean | 435 | 229 | 332 |

The larger amount of zirconium used for retanning caused significantly less deterioration, the average values for the two levels being: 4% zirconium tanning salt lost 391 lb./in. (14%) and 7% zirconium tanning salt lost 272 lb./in. (9%).

The application of a syntan topping reduced the deterioration, the complex aluminium salt being less effective. The average losses for the four groups are : no syntan topping 471 lb./in. (16%), 1% neutral syntan

207 lb./in. (7%), 1% replacement white syntan 317 lb./in. (11%) and complex aluminium salt 333 lb./in. (12%).

A non-ionic oil emulsion added during the zirconium retannage improved the durability of the grain. The application of cationic oil emulsions were not satisfactory. The average values for these leathers are: no addition of oil lost 373 lb./in. (13%), 1% cationic oil emulsion 440 lb./in. (15%), 0.5% cationic oil emulsion 302 lb./in. (11%), and non-ionic oil emulsion 213 lb./in. (7%).

Difference in Lastometer Extension at Grain Crack on Accelerated Ageing

The average reduction of the grain extension was 1.45 mm., but since the original extension of the grain was 12.03 mm. the deterioration is not serious.

The use of a chrome stable fatliquor materially reduced the deterioration but this was only effective at the high level of zirconium retannage. This interaction is given in Table IV.

Table IV
Fall in Lastometer Extension on Accelerated Ageing, (mm.)

| | Chrome-Stable Fatliquor | | |
|---|---|---|---|
| | none | sulphited oil | Mean |
| 4% zirconium | 1.61 | 1.67 | 1.64 |
| 7% zirconium | 1.53 | 0.99 | 1.26 |
| Mean | 1.57 | 1.33 | 1.45 |

The use of a non-ionic oil emulsion during the zirconium tannage reduced the deterioration, but cationic fatliquors were without effect. The average results for the four groups are: leathers with no oil added during the retannage lost 1.54 mm., 1% cationic oil fatliquor lost 1.51 mm., 0.5% cationic oil lost 1.52 mm., and 1% non-ionic emulsified oil lost 1.24 mm.

The use of a neutralised syntan in topping the leather after retannage caused less deterioration of the grain extension than either the replacement white syntan or the complex aluminium salt, both of which were without effect. The average losses for the four groups of leather are: no syntan topping 1.79 mm., 1% neutralised syntan 0.92 mm., 1% replacement white syntan 1.58 mm., and 1% complex aluminium salt 1.54 mm.

Incorporation of a buffering agent in the neutralising reduced the deterioration; leathers neutralised with sodium bicarbonate lost 2.01 mm. and those neutralised with sodium acetate and sodium bicarbonate lost 0.91 mm.

Difference in Lastometer Extension at Grain Crack on Natural Ageing

The average loss of extensibility on natural ageing was 1.54 mm., slightly greater than that obtained on accelerated ageing.

The main influence on the deterioration was due to the chrome tannage, the higher level of chrome giving more durable leather. This effect was influenced by the use of citric acid before zirconium retannage, and the interaction is given in Table V.

Table V
Fall in Lastometer Extension on Natural Ageing, (mm.)

| Pre-retan addition | Level of Chrome Tannage | | Mean |
|---|---|---|---|
| | 0.5% $Cr_2O_3$ | 2.0% $Cr_2O_3$ | |
| none | 1.66 | 1.68 | 1.67 |
| citric acid | 1.76 | 1.06 | 1.41 |
| Mean | 1.71 | 1.37 | 1.54 |

The level of chrome tannage was not significant on accelerated ageing but the trend was similar to that found on natural ageing.

The use of a syntan topping especially if the syntan was a neutralised syntan reduced the deterioration on storage. The influence of the complex aluminium salt for topping had no effect. The average results of the four groups are: leathers with no syntan topping lost 1.81 mm., 1% neutralised syntan lost 1.25 mm., 1% replacement syntan lost 1.48 mm., and 1% complex aluminium salt lost 1.62 mm.

The addition of a cationic oil emulsion during the zirconium retannage had no beneficial effect but a non-ionic oil emulsion reduced the deterioration. The influence of the various additions are illustrated by the following average results. Leathers with no oil added during the retannage lost 1.56 mm., with 1% cationic oil fatliquor lost 1.71 mm., with 0.5% cationic oil fatliquor lost 1.59 mm., and with 1% non-ionic emulsified oil lost 1.28 mm.

The higher amount of zirconium used for retanning caused less loss of extension than the smaller amount but this was only applicable when a chrome-stable fatliquor was used. This interaction is given in Table VI.

Table VI
Fall in Lastometer Extension on Natural Ageing. (mm.)

| | Chrome-Stable Fatliquor | | |
|---|---|---|---|
| | none | sulphited oil | Mean |
| 4% zirconium | 1.68 | 1.87 | 1.77 |
| 7% zirconium | 1.48 | 1.13 | 1.30 |
| Mean | 1.58 | 1.50 | 1.54 |

Difference in Acidity on Ageing

The average pH value of the leathers before ageing was 4.32. This was reduced to pH 4.16 on accelerated ageing and 4.18 on natural ageing. These differences of about 0.15 pH unit at that pH range constitute a negligible change in acidity. These leathers are therefore inherently chemically stable.

## DISCUSSION AND CONCLUSIONS

The most important observation from these results is that zirconium does not react with chrome tanned pelt in the same way that vegetable tannins do. Although tannage with zirconium may be due to reaction with basic groups in the hide and subsequent deposition within the fibre structure, there is no evidence of a subsequent reaction involving complex formation between zirconium and chromium. Leathers tanned with combinations of these two tanning agents are therefore less prone to deterioration than are leathers retanned with vegetable tannins.

Some deterioration occurred on ageing but it was significant that increasing amounts of zirconium retanning salt reduced the deterioration, indicating increased stability with increasing degrees of retannage.

increasing the chrome content also increased the durability. These two factors, namely high chrome content and high degree of retannage are particularly harmful in chromium/vegetable combination tannages.

Several ancilliary processes have been shown to affect the stability of the leather on ageing. Most important are those which involve the use of complexing or buffering agents. Although their effect cannot be explained in simple terms, the presence of these materials in leather is certainly beneficial.

The use of cationic fatliquors in the zirconium retannage was advantageous in the preparation of the leathers but they confer no increased durability on storage. On the other hand, a non-ionic emulsified oil added in conjunction with the zirconium improved the storage stability of the leathers. In the same way a chrome-stable fatliquor was beneficial when leathers were more heavily tanned.

Syntan toppings were rather disappointing, especially with regard to their effect on the grain. Only the neutralised syntan was significantly effective but the two speciality compounds - a replacement type white syntan and a complex aluminium salt - were ineffective.

In general, combination tannages involving chromium and zirconium give leather with a good handle and excellent physical properties, and are stable even under the most rigorous ageing conditions.

## REFERENCES

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# R.B. 320. THE RETANNAGE OF CHROME LEATHER WITH MINERAL TANNING AGENTS

by

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## SUMMARY

Complex zirconium and aluminium salts have been used in conjunction with chromium for preparing combination mineral tanned leather. The tanning agents can be applied together or in two separate stages but the results of this experiment indicate that there is no real difference between the two processes. Other factors included the degree of liming, the type of deliming material used, the amount of chrome offered, the type of neutralising alkali and the type of fatliquor oil.

Retannage with zirconium or aluminium retanning agents resulted in improved fullness and tightness, increased thickness and firmness, but the physical properties have not suffered. The average increase in thickness was of the order of 7%. Adjusting the process to give a higher chrome content also yielded thicker leather but the slit tear strength was slightly reduced.

Extending the liming time was not beneficial; although the extensibility and strength of the grain was improved, looseness was increased and thinner, emptier leather resulted. The type of neutralising material was unimportant.

Oil added during the retannage increased the flexibility, but the final fatliquor was more important in determining the properties. The cationic oil resulted in more extractable fatty matter and stronger but firmer leather, whereas the sulphated oil gave lighter more even coloured leather.

It is concluded that leathers of improved substance and a good round feel can be produced by a combination mineral tannage without adversely affecting the physical properties of the leather.

## INTRODUCTION

Zirconium has often been recommended for the retannage of chrome tanned leather when filling is required but the mineral characteristics must be retained. The manufacturers and suppliers of zirconium tanning salts have given starting formulations but these are not always entirely satisfactory.

In a previous publication from this Institute [1] a survey was made of a process [2] which was being applied successfully to calf skins in commercial production. The process enabled the leather to be paste dried yet it was claimed that the mineral characteristics were retained. In that survey using only one type of zirconium salt, these claims were largely confirmed, and the present work was undertaken to investigate other mineral tanning agents and to determine the degree of filling achieved with each. Other factors which it was thought might influence the results were included and these are given in detail below.

## EXPERIMENTAL

### Plan of the Experiment

The experiment was planned as a ¼ replicate of a $2^{10}$ factorial giving 256 treatment combinations. The factors varied and the levels of the factors were as follows:-

A Duration of Liming

- (1) ordinary sulphide lime
- a ordinary plus 3 days in white lime

BC Deliming Material

- (1) 1% ammonium chloride
- b 1.5% ammonium sulphate
- c 1% formic acid
- bc 1% acetic acid

D Amount of Chrome Offered

- (1) 1.5% $Cr_2O_3$
- d 2.5% $Cr_2O_3$

E Period at which Retannage Offered

- (1) during chrome tannage
- e after chrome tannage in fresh float

FG Type of Retanning Material

- (1) none
- f 4% complex aluminium salt, 1% $Al_2O_3$
- g 3.5% zirconium tanning salt A, 1% $ZrO_2$
- fg 4% zirconium tanning salt B containing silica, 1% $ZrO_2$

H Addition of Cationic Fatliquor during Retannage

- (1) none
- h 1% raw neatsfoot oil emulsified with 5% cationic and 1% non-ionic surface active agents

J Type of Neutralising Material

- (1) 1% sodium bicarbonate
- j 1% sodium acetate plus 1% sodium bicarbonate

K Type of Final Fatliquor

- (1) 4% raw neatsfoot oil emulsified with 5% cationic and 1% non-ionic surface active agent
- k 5% sulphated neatsfoot oil plus 2% non-ionic surface active agent on oil weight.

Process Details

Sixteen limed calfskins were cut into 16 samples each, giving a total of 256 specimens. These samples were sorted for factor A and those which were to receive the extra liming were transferred to a white lime for three days.

Each of the above groups were processed as follows at the appropriate time.

The samples were sorted for factor BC and delimed with the appropriate material for 30 minutes at 35$^{o}$C. 1% of a pancreatic enzyme bate was added and agitation continued for a further 30 minutes.

The samples were sorted for factor D and each was floated in 100% water and 5% salt. To the (1) samples was added 0.6% sulphuric acid and to the d samples 0.5% sulphuric acid. After 1 hour, the requisite quantity of chrome tanning salt dissolved in 25% water was added to the pickle liquors and drumming continued for 4 hours. The chromed pelt was sorted for factor E and the e samples removed with half the float and stored over-night. The no-e samples were sorted for factors FG and H and the liquor divided into 8 equal aliquots. To the samples in each were added the requisite type and quantity of retanning material as specified in factor FG and cationic fatliquor added according to factor H. Drumming was continued for 3 hours and the specimens left in the liquor over-night. On the following day the pH of each tannage was adjusted to 3.5 with sodium bicarbonate.

The e samples were drummed for several hours during which time the pH was raised to 3.7 by the addition of sodium bicarbonate. The exhaust chrome liquor was drained off and the specimens sorted for factors FG and H. The samples were floated in 125% water and the pH adjusted to 3.0 by the addition of sulphuric acid. The requisite type and quantity of retanning material was added according to factor FG and cationic fatliquor according to factor H. Retannage was continued for 3 hours when the pH was raised to 3.5 with sodium bicarbonate.

The leathers were piled over the weekend, then sorted for factor J, washed, neutralised with the requisite neutralising material, rewashed and dyed. They were resorted for factor K and fatliquored in a 100% float at 45°C for 45 minutes. The leather was horsed over-night, set out and dried.

After three weeks' conditioning the leathers were assessed for flexibility, looseness of the grain, depth and patchiness of colour, and fullness, before proceeding with physical tests and chemical analysis.

## RESULTS

### Analytical

The leathers were analysed in groups in order to characterise them. The leathers retanned with aluminium had an average $Al_2O_3$ content of 1.04%, and those retanned with zirconium A and B average $ZrO_2$ contents of 0.95% and 1.00% respectively.

Chrome was determined on four groups of leathers representing factors A and D. The average results are given below.

| Liming | Amount of Chrome Offered | | Mean |
|---|---|---|---|
| | 1.5% $Cr_2O_3$ | 2.5% $Cr_2O_3$ | |
| ordinary | 2.19 | 3.18 | 2.68 |
| ordinary + 3 days | 2.22 | 3.08 | 2.65 |
| Mean | 2.20 | 3.13 | 2.66 |

Fats and oils were determined on each leather by determining the difference in conditioned weight of the samples before and after exhaustive extraction with petroleum ether in a Davies extractor.

Only one factor, the type of final fatliquor, had a significant influence on the amount of extractable fats and oils. Less oil was extracted from those leathers fatliquored with sulphated oil than from those fatliquored with a cationic emulsion. Average results are: cationic oil, 5.4%; sulphated oil, 4.0%.

## Manual Assessments

### Flexibility

The flexibility of the samples was assessed manually and scores allocated from 0, soft to 7, firm.

There was a small but definite increase in stiffness on retanning with zirconium A and aluminium, the total scores for the four retannages being: no retannage, 100; aluminium, 109; zirconium A, 108; and zirconium B, 104.

The addition of a cationic oil during the retannage reduced the stiffness, the total scores for the two types being: no cationic fatliquor, 110; 1% cationic fatliquor during retannage, 100.

Increasing the duration of liming increased the stiffness but this was noticeable only when the leathers were retanned. This interaction is given in Table I.

Table I
Flexibility

| Liming | Type of Retanning Material | | | | Mean |
|---|---|---|---|---|---|
| | none | Al | Zr A | Zr B | |
| ordinary | 98 | 93 | 102 | 99 | 98 |
| ordinary + 3 days | 101 | 124 | 115 | 109 | 112 |
| Mean | 99 | 109 | 108 | 104 | 105 |

The stabilised sulphated oil fatliquor resulted in softer leather than the cationic fatliquor, average scores being: cationic fatliquor, 113; sulphated oil, 98.

Looseness of the Grain

Looseness was assessed visually and scores alotted on the scale 0, loose to 4, tight.

Retannage especially with aluminium and zirconium A improved the tightness of the leather. The scores for the four types of tannage were: no retannage, 79; aluminium, 106; zirconium A, 100; and zirconium B, 81.

Ammonium sulphate used in deliming resulted in tighter leather than that produced from any of the other three deliming agents between which there was no difference. The scores for each type are: ammonium chloride, 87; ammonium sulphate, 97; formic acid, 83; acetic acid 83.

Extending the period in lime resulted in looser leather. Ordinary liming, 60; ordinary plus 3 days, 54.

Depth of Colour

Colour was assessed visually and scores allocated on the scale 0, light to 6, dark.

Retannage with zirconium or with aluminium resulted in lighter colours, in particular zirconium B gave pale shades. Scores for the 4 retannages are: no retannage, 115; aluminium, 98; zirconium A, 95; zirconium B, 81.

The type of deliming material was also important, the ammonium salts giving lighter leather than the acids. Scores for the 4 deliming agents are: ammonium chloride, 92; ammonium sulphate, 85; formic acid, 107; acetic acid 105.

Longer liming resulted in much lighter colour giving a score of 76 against 116 for those that had had the shorter liming.

The addition of oil during the retannage gave darker leather than those tanned in the absence of oil. Scores for the two groups are: no oil in tannage, 92; 1% cationic oil, 101.

The most important factor was the type of final fatliquor, the stabilised sulphated oil giving very much lighter leather than that fatliquored with a cationic fatliquor. Scores for the two levels of this factor are: cationic fatliquor, 122; sulphated oil, 71. However, the fatliquors reacted differently depending on the type of retannage, the above effect being particularly noticeable on those samples retanned with zirconium. This interaction is given in Table II.

Table II
Depth of Colour

| Fatliquor | Type of Retanning Material | | | | Mean |
|---|---|---|---|---|---|
| | none | Al | Zr A | Zr B | |
| cationic oil | 144 | 112 | 116 | 116 | 122 |
| sulphated oil | 84 | 84 | 72 | 44 | 71 |
| Mean | 114 | 98 | 94 | 80 | 96 |

Patchy Dyeing

The specimens were assessed visually for unlevel dyeing and allocated scores on the scale 0, level to 3, patchy.

The type of deliming material influenced the levelness of dyeing, the acids being prone to give patchiness especially after the longer liming. Increase in the duration of liming also resulted in more patchy leather. The interaction is given in Table III.

Table III
Patchy Dyeing

| Liming | Deliming Material | | | | Mean |
|---|---|---|---|---|---|
| | $NH_4Cl$ | $(NH_4)_2SO_4$ | Formic | Acetic | |
| ordinary | 13 | 10 | 10 | 12 | 11 |
| ordinary + 3 days | 16 | 16 | 18 | 23 | 18 |
| Mean | 14 | 13 | 14 | 18 | 15 |

The type of retanning material influenced the patchiness, the retanning materials, especially aluminium, giving less level dyeing. The scores for the four processes are: no retannage, 12; aluminium, 18; zirconium A, 16; zirconium B, 13.

The type of final fatliquor resulted in a significant difference, the stabilised sulphated oil giving a more even colour. Scores for the two oils are: cationic oil, 16; sulphated oil, 13.

Shade

Although the leathers were all dyed together, quite different shades of colour were evident and it was possible to sort into 5 categories according to colour. The dye was a greenish yellow and the groups were allocated scores on the scale 0, yellow to 4, greenish yellow.

The longer liming resulted in a greener colour especially if followed by formic or acetic acid deliming. No difference in deliming material was noted for the shorter liming period. This interaction is given in Table IV.

Table IV
Shade

| Liming | Deliming Material | | | | Mean |
|---|---|---|---|---|---|
| | $NH_4Cl$ | $(NH_4)_2SO_4$ | Formic | Acetic | |
| ordinary | 11 | 10 | 7 | 8 | 9 |
| ordinary + 3 days | 10 | 8 | 18 | 24 | 15 |
| Mean | 10 | 9 | 12 | 16 | 12 |

A final fatliquor with cationic oil gave stronger leather than fatliquor with sulphated oil. Average figures are: cationic oil, 2174 lb./in.; sulphated oil, 2020 lb./in.

It is interesting to note that retannage with the mineral tanning agents used in this experiment did not significantly reduce the grain strength. Average results for the four processes are: no retannage 2161 lb./in.; aluminium, 2010 lb./in.; zirconium A, 2024 lb./in.; zirconium B, 2094 lb./in.

Lastometer Extension at Grain Crack

The factors varied in this experiment had very little influence on the extension at grain crack.

Extending the liming increased the extensibility from 10.5 mm. to 10.9 mm.

Retannage slightly reduced the extension at grain crack but this was dependent on the period at which the retannage was added. This interaction is given in Table VIII.

Table VIII
Extension at Grain Crack (mm.)

| Retannage | Type of Retanning Material | | | | Mean |
|---|---|---|---|---|---|
| | None | Al | Zr A | Zr B | |
| during Cr | 10.9 | 10.3 | 10.3 | 10.0 | 10.5 |
| after Cr | 11.1 | 10.6 | 10.8 | 11.0 | 10.9 |
| Mean | 11.0 | 10.5 | 10.6 | 10.5 | 10.7 |

The higher amount of chrome offered resulted in slightly less extensible leather, the average results being: 1.5% $Cr_2O_3$, 10.9 mm.; 2.5% $Cr_2O_3$, 10.5 mm.

The addition of fatliquor during the retannage increased the extension but the type of final fatliquor had no influence. Average results are: no oil added during retannage, 10.5 mm.; oil added during retannage, 10.9 mm.

Slit Tear Strength

Extending the duration of liming increased the slit tear strength, average results being: ordinary lime, 450 lb./in.; ordinary plus 3 days white lime, 500 lb./in.

The higher amount of chrome resulted in weaker leather, 1.5% $Cr_2O_3$, 498 lb./in.; 2.5% $Cr_2O_3$, 453 lb./in.

Adding the retannage after chrome tannage gave stronger leather than when the two tannages were combined. Retannage added during chrome tannage, 456 lb./in.; retannage added after chrome tannage, 494 lb./in. The type of retannage had no influence on the strength of the leather. Average results are: no retannage, 481 lb./in.; aluminium, 485 lb./in.; zirconium A, 450 lb./in.; zirconium B, 484 lb./in.

Shrinkage Temperature

The factor that had the most significant effect was the amount of chrome offered, the low chrome giving a Ts of 111°C and the high chrome 123°C.

The retannage had very little influence although aluminium increased the shrinkage temperature by a significant amount especially if applied in admixture with the chrome, and retannage with zirconium reduced the hydrothermal stability. This interaction is given in Table IX.

Table IX
Shrinkage Temperature, °C

| Retannage | Type of Retannage | | | | Mean |
|---|---|---|---|---|---|
| | None | Al | Zr A | Zr B | |
| during Cr | 117 | 126 | 119 | 116 | 120 |
| after Cr | 115 | 120 | 112 | 111 | 114 |
| Mean | 116 | 123 | 116 | 114 | 117 |

## DISCUSSION AND CONCLUSIONS

Increasing the duration of liming by three days in white lime in most cases was not beneficial. Looser leather and a more patchy dyed surface resulted. The leather was less full and thinner, but grain extension and grain strength and slit tear were improved.

The type of deliming material influenced the looseness; ammonium salts were better than the organic acids, resulting in tighter leather, pale even colour of dye and improved physical properties.

The amount of chromium was of little importance although the higher level resulted in thicker leather with a higher shrinkage temperature, but a slightly lower slit tear strength.

The most important factor was the type of retannage. This influenced most of the measured properties and was in most cases beneficial. Although the firmness of the leather was increased by the combination tannage, the grain was tightened, the leather was thicker and more full yet there was no significant loss of strength although the extension at grain crack was slightly reduced. Retannage with the aluminium tanning material appears to have given the best results, but zirconium is also very good.

Little difference was noted when the retanning was performed during the chrome tannage or as a separate process after chrome tannage. Slightly fuller leather was obtained by the former process but the thickness was hardly affected. On the other hand, superior physical properties were obtained when the retanning material was added after the chrome tannage but the effects were so small that no clear cut decision can be made in favour of either process.

The application of a cationic oil during the retanning process was important only as far as the stiffness and the aesthetic properties of the leather were concerned. In large-scale drum loads the oil may serve a useful purpose in reducing the build-up of frictional heat, although the oil may be responsible for differences in colour.

The type of alkali used for neutralising was relatively unimportant, the addition of the sodium acetate buffer salt giving slightly improved feel except for those leathers retanned with the complex aluminium salt.

The type of final fatliquor was important, the cationic oil resulting in a higher extractible oil content but firmer leather. The stabilised sulphated oil gave light even-coloured dyed surface of a purer yellow. Since the oil was applied after dyeing these effects must be physical, and related to the distribution of the oil at the surface. Thickness was not influenced by

# R.B. 366. AGEING CHARACTERISTICS OF MINERAL COMBINATION TANNED LEATHERS

by

D.A. Williams-Wynn, U. Jaeger & R. Dalling.

## SUMMARY

An investigation has been made of the ageing characteristics of chrome tanned leather retanned with aluminium or zirconium tanning salts. Ageing was conducted for four weeks under conditions of moist heat or for nine months under standard conditions.

None of the leathers was seriously affected by ageing and in some cases, especially among the full-chrome leathers, gains in strength were recorded. Optimum conditions for the combination tannage appear to be achieved if the retanning agent is added to the chrome liquor and a small amount of stable oil is included during the tannage. A mixture of sodium acetate and sodium bicarbonate is a better neutralising agent than sodium bicarbonate used alone for neutralising the combination tanned leathers, and a stabilised sulphated oil emulsion is superior to a cationic emulsified oil for fatliquoring these leathers.

## INTRODUCTION

Chromium/zirconium combination tanned leathers have been shown to have excellent ageing properties [1], and the strength characteristics of the leathers are good. In a subsequent experiment [2] various mineral tanning materials were compared as retanning agents for chrome tanned pelt. The present report considers the ageing properties of those leathers after both accelerated and natural ageing.

Details of the preparation of the leathers were given in the previous section.

## RESULTS

The results for the various properties are given as differences from the original. Only the strength characteristics have been reported since no chemical changes were detected. Generally speaking very few of the factors made significant differences to the storage stability of the leathers whether stored under conditions of moist heat or aged naturally.

## Lastometer Load at Grain Crack

### Accelerated Ageing

After ageing for three weeks at 48°C and 95+% r.h. these leathers had lost on average only 38 lb./in., which on the original strength of the leathers represents a fall of only 1.9%. Few of the factors influenced this deterioration, but one of the most important was the type of fatliquor. Those leathers lubricated with the cationic fatliquor lost almost twice as much as those fatliquored with ordinary sulphated oil. The average losses of strength for these two processes are: cationic oil, 50 lb./in.; sulphated oil, 27 lb./in.

Of the mineral retanning materials, only the aluminium resulted in increased deterioration, the losses for the two zirconium salts being very slightly less than the deterioration of the full-chrome leather. However, the differences are dependent on the period at which the retanning material was added, the optimum being when the retanning material is added with the chrome. This interaction is given in Table I.

Table I
Fall in Load at Grain Crack, (lb./in.)

| Period | Mineral Retannage | | | | Mean |
|---|---|---|---|---|---|
| | None | Al | Zr A | Zr B | |
| during chrome | 38 | 40 | 17 | 31 | 31 |
| after chrome | 38 | 52 | 48 | 42 | 45 |
| Mean | 38 | 46 | 32 | 36 | 38 |

When the mixed neutralising agent was used less deterioration was found with the mineral retanning materials than when sodium bicarbonate alone was used for neutralising. On the other hand, full-chrome leathers deteriorated less when sodium bicarbonate was used. This interaction is given in Table II.

Table II

Fall in Load at Grain Crack (lb./in.)

| Neutralisation | Mineral Retannage None | Al | Zr A | Zr B | Mean |
|---|---|---|---|---|---|
| Na $HCO_3$ | 27 | 62 | 42 | 38 | 42 |
| Na acetate + Na $HCO_3$ | 49 | 30 | 23 | 35 | 34 |
| Mean | 38 | 46 | 32 | 36 | 38 |

Natural Ageing

On natural ageing the loss of strength was only 21 lb./in. The effect of the fatliquor was similar, but the difference between the two types was less and not significant. As with the accelerated ageing, the application of the mineral retanning materials after the chrome tannage resulted in greater deterioration. These values are given in Table III.

Table III

Fall in Load at Grain Crack (lb./in.)

| Period | Mineral Retannage None | Al | Zr A | Zr B | Mean |
|---|---|---|---|---|---|
| during chrome | 12 | 20 | 2 | 13 | 12 |
| after chrome | 16 | 40 | 29 | 40 | 31 |
| Mean | 14 | 30 | 15 | 27 | 21 |

Less deterioration occurred in the combination tanned leathers when the mixed neutralising material was used, but this procedure caused greater deterioration in the full-chrome leathers. This interaction is given in Table IV.

Table IV

Fall in Load at Grain Crack (lb./in.)

| Neutralisation | Mineral Retannage None | Al | Zr A | Zr B | Mean |
|---|---|---|---|---|---|
| Na $HCO_3$ | 10 | 32 | 18 | 26 | 22 |
| Na acetate + Na $HCO_3$ | 19 | 27 | 12 | 27 | 21 |
| Mean | 14 | 30 | 15 | 27 | 21 |

## Lastometer Extension at Grain Crack

### Accelerated Ageing

The extension at grain crack fell by an average of 0.76 mm., and since the original average extension was 10.7 mm, this does not represent a serious loss.

The type of retannage affected the results, the full-chrome leathers losing more than the combination tanned leathers. Average losses for the four tannages are: full-chrome, 0.95 mm., aluminium, 0.84 mm., zirconium A, 0.56 mm., zirconium B, 0.68 mm. The sulphated oil fatliquor caused less deterioration than the cationic emulsified oil fatliquor, the loss in extension being 0.62 mm. and 0.90 mm. respectively.

### Natural Ageing

On natural ageing the average fall in extension was only 0.36 mm.

Of the retannages, aluminium combination tanned leathers suffered most, losing 0.55 mm, compared with 0.40 for the full-chrome leathers, and 0.15 and 0.37 for leathers retanned with zirconium A and zirconium B respectively. The sulphated oil fatliquor resulted in less deterioration than the cationic emulsified oil fatliquor, the loss in extension being 0.22 mm. and 0.51 mm. respectively. The addition of a small amount of cationic oil during the retannage also resulted in less deterioration, those leathers that had not been treated with oil losing 0.51 mm. and those retanned in the presence of oil lost 0.22 mm.

## Slit Tear Strength

### Accelerated Ageing

The loss of strength on accelerated ageing was negligible, the average fall being only 4 lb./in. This low figure was obtained because the full-chrome leathers tended to gain in strength, whereas the combination tanned leathers deteriorated slightly. Full-chrome leathers gained an average of 12 lb./in., whereas the aluminium leathers lost 5 lb./in., zirconium A leathers 9 lb./in., and zirconium B leathers 18 lb./in. The cationic oil fatliquored leathers lost an average 17 lb./in., whereas the sulphated oil fatliquored leathers gained 8 lb./in.

Natural Ageing

On natural ageing the leathers gained an average of 2.5 lb./in. in tearing strength and none of the factors significantly influenced the change in strength.

## DISCUSSION AND CONCLUSIONS

The ageing characteristics of the mineral combination tanned leathers were excellent. None of the factors resulted in very large differences, so the choice of tanning technique will depend largely on convenience and handling. Some benefit was derived from retanning in the chrome liquor, but the improvements were so small that the problem of the larger volume of effluent associated with the alternative process is probably a more significant deciding factor.

In the manufacture of combination mineral tanned leather, a suitable process would be to lime and pickle in the normal manner, to add the chrome tanning salt to the exhaust pickle liquor and after a few hours to add the dry zirconium or aluminium tanning salt. After tanning for several hours, the liquor should be basified slowly to a pH of approximately 4. Neutralising and fatliquoring can be effected after the usual mechanical treatments, a mixed neutralising agent being superior to sodium bicarbonate used alone. In fatliquoring, a conventional sulphated oil fatliquor is normally quite satisfactory, but if it tends to be unstable the addition of a small amount (5% on the weight of the oil) of a non-ionic surface active agent will improve the stability.

Lime splitting is recommended since the hard nature of the combination tanned leathers tends to blunt the splitting knife. In addition, lime splitting ensures a more even distribution of the retanning agent.

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# PART II

## RETANNAGE OF CHROMIUM TANNED LEATHER WITH VEGETABLE TANNING EXTRACTS

# R.B.-206. A NOTE ON RAPID TEST METHODS FOR PREDICTING THE DURABILITY OF CHROME/VEGETABLE TANNED LEATHERS

by

R.L. Sykes and D.A. Williams-Wynn.

## SUMMARY

Methods for predicting the durability of combination chrome/vegetable tanned leathers have been compared. Deterioration appears to be associated with an increase in the acidity of the leather. The Innes Peroxide Test and accelerated ageing at 50°C and 95+% r.h. give very similar predictions as to durability, which are however only accurate for leathers containing small amounts of organic anions. The presence of comparatively large amounts of masking agent produces a more stable leather, probably by its protecting action on the chromium complex.

## INTRODUCTION

Correspondence in the Journal[1,2] on rapid test methods for predicting the durability of chrome-retanned upholstery leathers either by the Innes Peroxide Test or by other methods has raised a problem of much wider interest than may have been envisaged by Heal when he wrote his original letter[1]. Work in these laboratories during the past 3 years has been concerned with the problem of deterioration of chrome-retan side leathers and, since it appears that in many cases the acidity plays an important role, it was felt that publication of an interim progress report on some of our findings may be of value to those interested in any aspect of the stability of combination tanned leathers.

Publications originating from the U.S.A.[3-6] have shown that chrome-retan leather is relatively unstable in temperate and tropical climates, and in some of these papers mention is made of a fall in the pH of chrome-retan leathers which had lost strength during storage. Roddy and Jansing stored leathers in humid atmospheres for a period of 16 weeks and found that in some cases the tensile strengths were halved after this accelerated ageing. As there was no data available on the decrease in strength of these leathers when aged for longer periods under more equable conditions, experiments have been carried out to compare the rate of deterioration of chrome-retanned leather under a variety of conditions.

## DEVELOPMENT OF ACCELERATED AGEING TEST FOR RETAN LEATHER

In a preliminary experiment, chromed stock was retanned with 16.7% wattle extract prior to dyeing, fatliquoring and drying. Nine lots of four replicate samples were cut from the hide and each lot of replicates was stored under one of the following conditions of temperature and humidity, 20, 40 and 55°C and 65, 85 and 95+% relative humidity. Test pieces were cut from each sample at various time intervals and tested for buckle tear strength and load at grain crack, and the pH of a 5% aqueous extract was determined. The experiment ran for eight months, after which final tests were made. The leathers stored at 55°C and 95+% r.h. were embrittled after a month or so and had lost much of their strength, whilst the leathers stored under standard conditions, 20°C and 65% r.h. for 8 months or more were still in reasonably good condition visually, although the buckle tear strength had dropped by 25% and the load at grain crack by 40%. The more stringent conditions, particularly high relative humidity, led initially to a fall in the pH of an aqueous extract of the leather, although this began to rise on more prolonged storage, a point which is dealt with more fully below. This work had as its objective the development of a fairly rapid test for the extent of deterioration that chrome retan upper leather might undergo in a 6-12 month period prior to use in footwear factories, and it appeared that storage for 3 weeks at 50°C and 95+% r.h. (Maximum humidity in Gallenkamp Humidity Cabinet) would bring about the same amount of deterioration as 8-9 months storage at 20°C and 65% r.h. The validity of this assumption particularly with respect to buckle tear strength has subsequently been confirmed in tests carried out on many samples of retan leathers produced commercially or for experimental purposes. Two sets of figures are quoted below in support of this statement (Table I); divergent results have been found for certain leathers and will be discussed later.

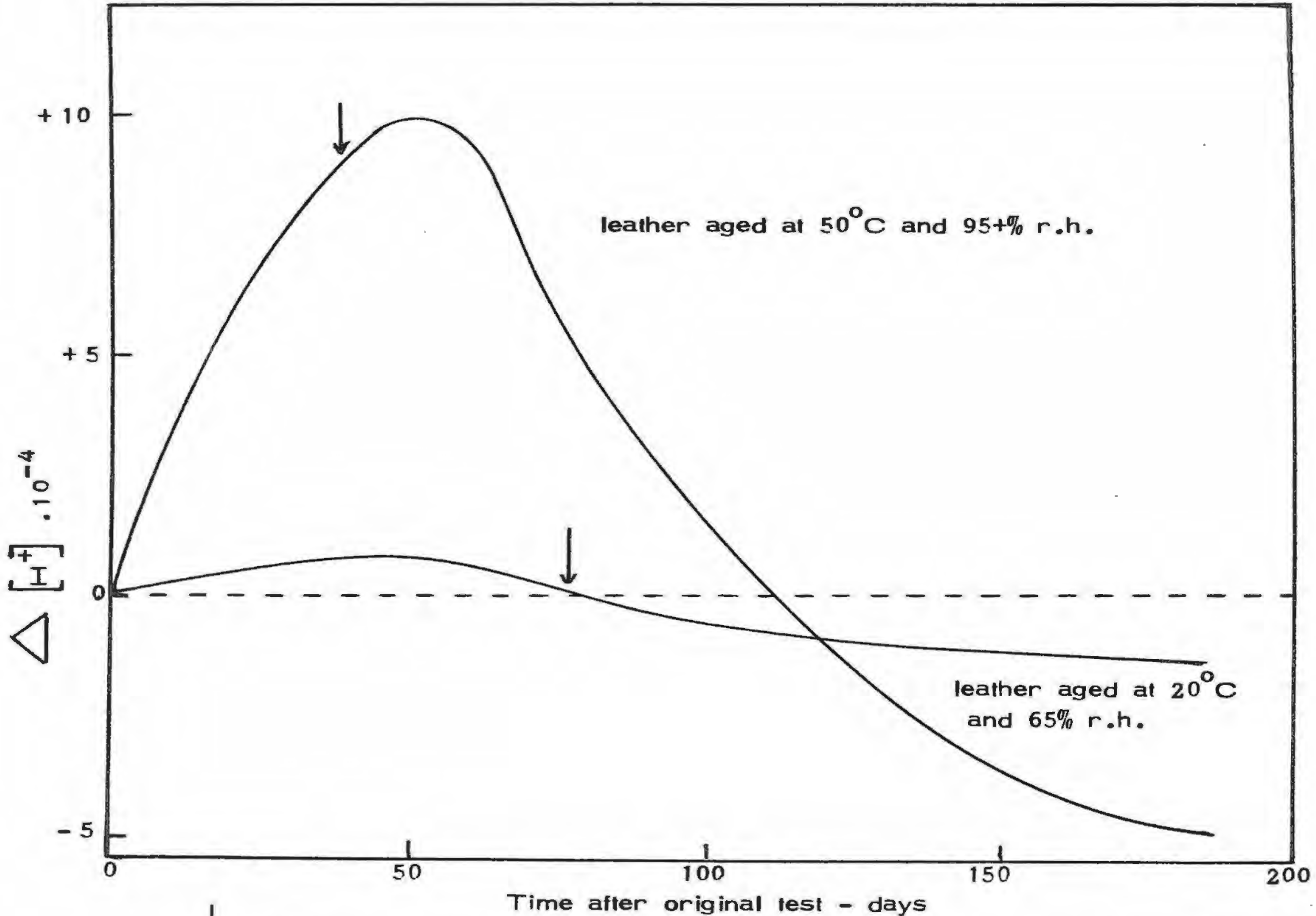
Table I

Changes in the Strength of Chrome-Vegetable Retan Leather After Storage

| | Lot A<br>6 samples from one pack commercial side leathers retanned with wattle | | Lot B<br>10 samples experimental goat leathers retanned with quebracho, sumac and wattle at different pH levels |
|---|---|---|---|
| | Buckle Tear | Lastometer Grain crack | Buckle Tear |
| Original test (2-3 weeks after manufacture) | 1017 lb./in. | 751 lb./in. | 540 lb./in. |
| Fraction of original strength retained after accelerated ageing for 3 weeks at 50°C and 95+% r.h. | 90.3% | 74.0% | 71.5% |
| Fraction of original strength retained after normal ageing for 8 months at 20°C and 65+% r.h. | 90.5% | 84.7% | 70.3% |

## EFFECT OF INITIAL pH ON EXTENT OF DETERIORATION

While the work referred to above was being carried out it was observed that leathers which were initially somewhat acidic in character tended to deteriorate most rapidly. Accordingly a series of wattle-retan leathers was prepared to have a range of acidities. The initial strengths of these leathers varied quite considerably so the results were calculated as percentage deterioration after 8 months storage at 20°C and 65% r.h. and these are given in Table II.




↓ indicates first positive reaction with ninhydrin for protein degradation products.

Figure 1. Relationship between acidity of queous extract of leather and age.

Table II
Relationship Between Extent of Deterioration and Initial pH of Leather

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH of 5% aqueous extract of original leather | 4.44 | 3.68 | 3.29 | 3.19 | 3.13 | 3.11 | 3.09 | 3.05 | 3.03 | 3.00 | 2.83 | 2.70 |
| % drop in buckle tear strength after storage for 8 months at 20°C and 65% r.h. | 0 | 6 | 7 | 29 | 34 | 29 | 23 | 40 | 22 | 38 | 29 | 33 |

It therefore appears that the acidity of a retan leather after manufacture is likely to play a very important role in its stability; this finding agrees with the conclusions drawn by Lollar [7].

## CHANGES IN THE ACIDITY OF RETAN LEATHER ON STORAGE

The pH of a 5% aqueous extract of chrome leather retanned with quebracho, sumac and wattle extracts was found to change when the leather was stored for prolonged periods. Initially there is a drop in the pH of the aqueous extract, but on prolonged storage the pH begins to rise, a phenomenon which has been found in the case of vegetable tanned leathers stored in acid atmospheres for prolonged periods [8]. The two graphs shown in Fig. 1 are typical of the changes in acidity which have been found for many retan leathers; one depicts the changes for a leather stored at 20°C and 65% r.h., the other a leather stored at 50°C and 95+% r.h. It has been reported that, in the case of vegetable tanned leathers, the increase in pH is brought about by degradation of the protein [8]. A simple test with ninhydrin on the aqueous extracts of chrome retan leathers demonstrated the presence of protein degradation products after prolonged storage. The point at which a positive test for protein degradation products was first obtained is shown on the graphs.

## COMPARISON OF WARM HUMID STORAGE WITH INNES PEROXIDE TEST

Although in many instances excellent correlation has been obtained between the changes in strength which occur during natural storage and the accelerated ageing test described previously, it was found that some retan leathers did not show any deterioration when left at 20°C and 65% r.h. for periods of a year or more, but that they had shown some deterioration under the conditions of our accelerated ageing test. It was found that this is usually associated with a high content of organic anions in the leather, applied either as masking agents during tannage or in the neutralising process. Typical results are given below in Table III.

Table III

Deterioration of Leathers Retanned With 16.7% Wattle Extract Which Contain Large Amounts of Organic Anion

| Leather | Application of Organic Anion | Percentage loss of Buckle Tear strength after storing for 3 weeks at 50°C and 95+% r.h. | Percentage loss of Buckle Tear strength after storing for 8 months at 20°C and 65% r.h. |
|---|---|---|---|
| 1. | $2\frac{1}{2}$ mole formate/mole Cr as masking agent | 22 | 6 |
| 2. | $2\frac{1}{2}$ mole phthalate/mole Cr as masking agent | 42 | 7 |
| 3. | $2\frac{1}{2}$ mole sulpho-phthalate/mole Cr as masking agent | 34 | 0 |
| 4. | Neutralised with $\frac{1}{2}$% Na-formate and 2% neutral syntan on shaved wt. unmasked chrome tannage | 33 | 4 |
| 5. | Oxalato-chromiate tannage | 35 | 5 |

The use of the Innes Peroxide Test (9) was then considered, to determine whether it would be a more accurate guide to the storage stability of chrome-retan leathers (2-4% $Cr_2O_3$, retanned with 16.6% wattle extract) containing large amounts of organic anions. A total of 56 leathers were used in this comparison. The damage caused by the Innes Peroxide Test was scored from 0 - 4, where 0 indicated that no apparent damage had occurred and the leather after testing would still pass a double fold test without any sign of grain crack, whereas 4 indicated curling and visual embrittlement. The percentage fall in the lastometer load at grain crack after 3 weeks storage at 50°C and 95+% r.h. was also determined. Calculation of a correlation coefficient for the 56 pairs of results gave a value for $r = 0.335$ which is statistically significant at the 1% level, and indicates that there are some factors common to the mechanism of breakdown under the two different test methods. Results given in Table IV are average ones for 8 samples comparing the score on the Innes Test and the drop in grain strength after accelerated ageing for masked chrome tannages retanned with 16.7% wattle extract.

Table IV

Comparison of Innes Peroxide Test and Loss of Strength on Warm Humid Storage *

| Masking agent used in chrome tannage | Score on Innes Peroxide Test | Drop in load at grain crack after 3 weeks ageing at 50°C and 95+% r.h. |
|---|---|---|
| None | 2.75 | 690 lb./in |
| Formate | 2.62 | 590 " |
| Phthalate | 1.94 | 450 " |
| Sulphophthalate | 1.75 | 420 " |
| * Results quoted are means for 8 samples | | |

## DISCUSSION AND CONCLUSIONS

The deterioration of chrome-vegetable retan leather has been studied and it appears that it is associated with the formation of acidity, probably by displacement of strong acid anions from the chromium complex present in the leather, and is particularly noticeable if the original leather is comparatively acid in character. It seems that the use of buffer salts, all of which form stable chromium complexes, as masking or neutralising agents will reduce or even eliminate deterioration of chrome retan leather under temperate conditions. Accelerated ageing under warm humid conditions for a short period gives a degree of deterioration very similar to that found after a longer time under more equable conditions for chrome/vegetable leathers. Where large amounts of masking or buffer salts are present in the leather this accelerated ageing test gives spurious results in that it predicts deterioration which does not take place when the leather is stored in a standard atmosphere. It also appears that the stronger the masking action of the organic anion the more stable is the retan leather produced. A possible explanation for the breakdown at high temperature and humidity is that the weak acid anions have a peptising effect on the leather fibre similar to that found when sole leather is hot-pitted indiscriminately [(10)]. The Innes Peroxide Test although carried out at 20°C gave predictions for stability similar to the accelerated ageing test at 50°C. It is probable that with the much more acid condition of the leather under the Innes Test, the peptising effect is more pronounced at the lower temperature. It is therefore possible that the divergent results found by Heal for combination tanned upholstery leather may have a similar cause, and some further details as to the nature of the tannages which yielded divergent results may be of general interest.

While it is stressed that this work is as yet incomplete and that further work is in progress, it is hoped that the tentative conclusions drawn in this interim report will be of value to leather chemists interested in all aspects of the durability of chrome retan leathers.

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# R.B. 229. CHROME RETAN LEATHER : EFFECT OF MASKING ON STRENGTH AND DURABILITY - RELATIONSHIP BETWEEN ACCELERATED AND NATURAL AGEING

by

R.L. Sykes and D.A. Williams-Wynn.

## SUMMARY

A factorial experiment is described in which the effects of two properties of several masking agents on strength and durability of chrome retan leather were investigated. Other factors varied included pretanning processes, the amount of chrome offered, the degree of neutralisation and the period at which the fatliquor was offered.

The results indicate that masking increases the strength and durability, the efficiency of the various masking agents depending on the amount offered. Important observations with regard to the pretanning and fatliquoring processes were made and these require further study.

The accelerated ageing test is not completely satisfactory as a measure of the amount of deterioration to be expected on natural ageing when large amounts of organic acid anions are present. In the absence of organic acids the test gives a fairly accurate assessment of the amount of deterioration to be expected. The Innes Peroxide Test correlates strongly with the accelerated ageing test and as such cannot be used to estimate deterioration on natural ageing.

## INTRODUCTION

Several factorial experiments have been carried out [1-7] and methods for the manufacture of satisfactory strong retan leather are available. In addition a rapid test method for predicting the durability of chrome retan leather has been evolved [8], but this has not given a true indication of the stability of leathers which contain a high proportion of organic anions. The present work was undertaken for the express purpose of comparing the accelerated ageing test with both the Innes peroxide test and natural ageing. At the same time, factors which had not previously been varied in an experiment of this nature were included, together with factors which we knew would give large variations in strength and durability of the leather.

## EXPERIMENTAL

### Plan of the Experiment

#### Factors Varied, and Levels of the Factors

A Pretanning processes

(1) Warm lime, 30°C after unhairing
a Bated - 2% Pancreol 5 A, $\frac{1}{2}$ hr.

B Amount of chrome offered

(1) 5% Kromex
b 10% Kromex

C Amount of masking salt (amount depends on type)

(1) $\frac{1}{2}$ mole/mole $Cr_2O_3$
c $2\frac{1}{2}$ mole/mole $Cr_2O_3$

DE Type of masking salt

(1) none
d Formate
e Phthalate
de Sulphophthalate

F Neutralising
(1) none - good wash
f 1% $NaHCO_3$ - $\frac{1}{2}$h, washed.

G Period at which fatliquor offered

(1) Before vegetable retanning
g After vegetable retanning.

### Statistical Plan

The experiment was arranged as a $\frac{1}{2}$ replicate of $2^7$ factorial = 64 samples, cut from 8 blocks of 8 samples each. One first order interaction $\overline{ADE}$ was confounded with blocks.

### Preparation of the Samples

The samples were cut from four dry-salted calfskins, two blocks from each skin. The hair was removed by lime/sulphide paste in the drum and the pieces were sorted for factor A. One lot was put into white lime at ordinary temperature and then washed, surface delimed, and bated with 2% Pancreol 5A for $\frac{1}{2}$ h. The remainder were put into a warm lime (30°C) after unhairing, for the same length of time as the previous lot, 1/3 delimed but were not bated. The pieces were combined for pickling with 3/4% sulphuric acid, 5% salt, and 150% water for 2 hours, and then sorted for factors B C $\overline{DE}$, i.e., 16 different tannages. Tanning was performed in miniature glass tanning drums and no basifying was required. The type and amount of masking salt had a considerable influence on the final pH as shown in Table I.

Table I
pH of Exhaust Chrome Liquors

| Amount of masking agent | Masking Agent | | | | Mean |
|---|---|---|---|---|---|
| | None | Formate | Phthalate | Sulpho-phthalate | |
| (1) ½ mole | 3.80 | 3.75 | 3.70 | 3.75 | 3.75 |
| c 2½ moles | 3.80 | 4.65 | 4.30 | 4.10 | 4.24 |
| Mean | 3.80 | 4.20 | 4.00 | 3.93 | 3.98 |

After tanning, the pieces were sammed and piled for 2 days and then sorted for factor F. One lot was merely washed whereas the other was neutralised with 1% of sodium bicarbonate for ½ hour then thoroughly washed. The samples were resorted for factor G, one lot being fatliquored with 2½% sulphated whale oil and 2½% raw oil before retanning with 10% wattle extract for 40 min. The other lot was retanned first, then lubricated with the same fatliquor mixture. All the pieces were set out then pasted to dry.

## RESULTS

## PHYSICAL PROPERTIES OF ORIGINAL LEATHERS

### Lastometer Load at Grain Crack

In this experiment two factors influenced the load at grain crack to a considerable extent. The grain strength was much higher in the leather resulting from the warm lime than that which had been bated (warm lime 2237 lb./in.; bated samples 1706 lb./in.), and the low amount of chrome tanning salt produced stronger leather than the high amount (5% Kromex, 2113 lb./in.; 10% Kromex, 1830 lb./in.). The type of masking agent used also had a marked effect on the strength, but this was just significant at the 5% level. The samples which were tanned with unmasked chrome salts had a grain strength of 1797 lb./in.; formate masking gave a grain strength of 2048 lb./in.; phthalate masking, 2066 lb./in., and sulphophthalate masking, 1976 lb./in.

Lastomer Extension at Grain Crack

The extension at grain crack was not greatly affected by any of the variables in this experiment but four factors did have significant effects. After unhairing, the warm lime gave a greater extension (9.03 mm.) than did bating (8.79 mm.). The amount of chrome offered also affected the extensibility of the leather. Tannage with the small amount of chrome gave more extensible leather (9.08 mm.) than that tanned with the large amount of chrome (8.75 mm.). When the chrome liquor was masked the extension of the leather was reduced. The extensions for the four types of chrome tannage being, unmasked chrome, 9.20 mm.; formate masked 8.83 mm.; phthalate masked, 8.76 mm.; and sulphophthalate masked 8.86 mm. Fatliquoring after the vegetable retannage gave more extensible leather (9.06 mm.) than fatliquoring before retannage (8.77 mm.).

Buckle Tear Load

Only one factor greatly affected the strength of the leather as determined by the buckle tear test. The high amount of chrome offered considerably reduced the strength (10% Kromex, 383 lb./in.; 5% Kromex 471 lb./in.). The samples that had been given the warm liming after unhairing were stronger than those that were bated, but this effect is significant at only the 5% level, (warm lime 450 lb./in.; bate, 412 lb./in.). None of the other factors influenced the strength of the leather although a significant interaction indicated that the leather tanned with heavily masked chrome liquors should not be neutralised if optimum strength were desired. This is shown in Table II.

Table II
Buckle Tear Load, (lb./in.)

| Amount of masking agent | Neutralising | | Mean |
|---|---|---|---|
| | none | 1% $NaHCO_3$ | |
| ½ mole | 417 | 447 | 432 |
| 2½ moles | 461 | 386 | 423 |
| Mean | 439 | 416 | 427 |

Thickness

Thickness was influenced by the pretanning process, warm lime giving much thinner leather than bating (warm lime, 1.26 mm.; bate, 1.44 mm.). The amount of chrome tanning salt used also influenced the thickness, thicker leather was obtained with the large amount of Kromex (5% Kromex, 1.28 mm.; 10% Kromex, 1.42 mm.).

## CHANGES IN PHYSICAL PROPERTIES ON ACCELERATED AGEING

The only properties that are likely to change on ageing are buckle-tear strength, load at grain crack, and extension at grain crack. By determining changes in the physical properties, those factors which markedly alter the rate of deterioration on ageing are shown up. Accelerated ageing consisted of storage at 47°C and 95+% r.h. for 3 weeks, after which the leathers were dried out, conditioned and tested.

### Difference in Buckle Tear Strength between Artificially Aged and Unaged Leathers

Differences in the rate of deterioration are mainly associated with the type of masking salt, but no straight-forward assessment of the efficiency of the masking salts is possible. Interactions vary with the amount of masking salt used and the amount of chrome tanning salt offered. In general, the masking salts show up badly in this test, the amount of deterioration being greatest where the masking salts are present. However, the use of a large amount of formate prevents deterioration under the conditions of this test, see Table III.

Table III

Fall in Buckle Tear Strength on Accelerated Ageing, (lb./in.)

| Amount of masking salt | Type of Masking Salt | | | | Mean |
|---|---|---|---|---|---|
| | none | Formate | Phthalate | Sulpho-phthalate | |
| ½ mole/mole | 15 | 74 | 89 | 4 | 45 |
| 2½ moles | 30 | -6 | 30 | 79 | 33 |
| Mean | 22 | 34 | 60 | 41 | 39 |

Deterioration is greater when a large amount of chrome is used in the absence of masking agents, but a large drop in strength was found when the small amount of chrome was used in conjunction with masking salts. This interaction is given in Table IV.

Table IV

Fall in Buckle Tear Strength on Accelerated Ageing, (lb./in.)

| Amount of chrome offered | Type of Masking Salt | | | | Mean |
|---|---|---|---|---|---|
| | none | Formate | Phthalate | Sulpho-phthalate | |
| 5% Kromex | 12 | 26 | 95 | 95 | 57 |
| 10% Kromex | 33 | 39 | 24 | -12 | 20 |
| Mean | 22 | 33 | 60 | 41 | 39 |

The type of neutralising procedure also affected the amount of deterioration. The neutralised samples deteriorated less than the un-neutralised samples, (wash, no neutralisation, 62 lb./in.; neutralised, 16 lb./in.).

Difference in Load at Grain Crack between Artificially Aged and Unaged Leathers

Less deterioration occurred in the samples that had been neutralised compared with those that had only been washed, but this was evident only in the samples that had had the small amount of masking salt, see Table V.

Table V

Fall in Load at Grain Crack on Accelerated Ageing, (lb./in.)

| Amount of masking salt | Neutralising | | Mean |
|---|---|---|---|
| | none | 1% $NaHCO_3$ | |
| ½ mole | 720 | 400 | 560 |
| 2½ moles | 560 | 560 | 560 |
| Mean | 640 | 480 | 560 |

The type of chrome tannage influenced the amount of deterioration as determined by this test. Leathers that had been tanned with chrome masked with phthalate or sulphophthalate showed much less deterioration than those that had been tanned with formate masked or unmasked chrome. The loss in strength by each of the four tannages was: unmasked, 690 lb./in.; formate 590 lb./in.; phthalate, 450 lb./in.; and sulphophthalate, 420 lb./in.

Difference in Extension at Grain Crack between Artificially Aged and Unaged Samples

The reduction of the extension at grain crack of the samples which had been given the accelerated ageing treatment was about 0.8 mm. Since the average extension of the original leather was 8.91 mm., the extension had not been affected to any great degree and all samples were quite satisfactory in this respect. The only factor that had a large effect on the magnitude of the difference in extension was the amount of chrome offered. The samples which had been tanned with the large amount of chrome showed a smaller drop in extension than the others, (5% Kromex, 0.98 mm.; 10% Kromex, 0.57 mm.).

Another interesting effect is the interaction between the period at which the fatliquor had been added and the type of masking salt used, see Table VI. Whilst, on the average, all leathers deteriorated to approximately the same extent regardless of the masking agent employed, the amount of deterioration depended on the period at which the fatliquor was offered. In the case of the leathers that had had no masking salt offered, less deterioration occurred if the fatliquor was added before the vegetable retannage. This was also the case for the phthalate masked leathers, but for formate the reverse was the case and for sulphophthalate the period at which the fatliquor was added was unimportant.

Table VI

Fall in Extension at Grain Crack on Accelered Ageing, (mm.)

| Period at which fatliquor offered | Type of Masking Salt | | | | Mean |
|---|---|---|---|---|---|
| | None | Formate | Phthalate | Sulpho-phthalate | |
| before veg. | 0.4 | 1.1 | 0.5 | 0.6 | 0.6 |
| after veg. | 1.1 | 0.7 | 1.1 | 0.6 | 0.9 |
| Mean | 0.8 | 0.9 | 0.8 | 0.6 | 0.8 |

## CHANGES IN PHYSICAL PROPERTIES ON NATURAL AGEING

Natural ageing consisted of storage at 21°C and 65% r.h. for nine months after which time the samples were tested for buckle tear load, load at grain crack, and extension at grain crack. The results are given as differences from the original values.

### Difference in Buckle Tear Strength between Naturally Aged and Unaged Leathers

The differences in buckle tear strength between unaged and naturally aged leathers were not very big but several factors were shown to be significant. The interaction between the amount of chrome tanning salt offered and the type of masking salt used is important. In the absence of masking salt the deterioration with the large amount of chromium is greater than with the smaller amount offered, although the absolute values are small, see Table VII. Formate prevents deterioration at both levels of chromium, but phthalate and sulphophthalate prevent deterioration only with the large amount of chromium. The effect is complicated still further since the amount of masking salts added affects the degree of deterioration. The high proportion of formate and phthalate prevent deterioration and at the low level deterioration is quite extensive. With sulphophthalate the low proportion is most effective, whereas deterioration is not prevented with the high molar ratio see Table VIII.

Table VII

Fall in Buckle Tear Strength on Natural Ageing, (lb./in.)

| Amount of chrome offered | Type of Masking Salt | | | | Mean |
|---|---|---|---|---|---|
| | None | Formate | Phthalate | Sulpho-phthalate | |
| 5% Kromex | 22 | 11 | 86 | 76 | 49 |
| 10% Kromex | 29 | 13 | 10 | 6 | 14 |
| Mean | 25 | 12 | 48 | 41 | 31 |

Table VIII

Fall in Buckle Tear Strength on Natural Ageing, (lb./in.)

| Amount of masking salt | Type of Masking Salt | | | | Mean |
|---|---|---|---|---|---|
| | None | Formate | Phthalate | Sulpho-phthalate | |
| 0.5 mole | 19 | 42 | 91 | 14 | 41 |
| 2.5 mole | 32 | -19 | 5 | 69 | 22 |
| Mean | 25 | 12 | 48 | 41 | 31 |

The period at which the fatliquor was offered also influenced the rate of deterioration. Fatliquor offered after chrome tannage but before the vegetable tannage resulted in a lower amount of deterioration than if the fatliquor was added at the end of the tannage, i.e., after the vegetable tannin had been taken up. The average drop in strength of the samples that had the fatliquor before the vegetable tannage was 16 lb./in. and of the samples which were fatliquored after vegetable tannage, 47 lb./in.

Difference in Load at Grain Crack between Naturally Aged and Unaged Leathers

Of the factors varied, only the type of masking salt influenced the amount of deterioration, but the effect of the masking salts is dependent on he amount offered. This interaction is given in Table IX. The presence of nasking salts reduced the amount of deterioration but this is particularly vident at the high molar ratio. Only phthalate reduced the amount of eterioration to any marked extent at the low molar ratio.

Table IX

Fall in Load at Grain Crack on Natural Ageing, (lb./in.)

| Amount of masking salt | Type of Masking Salt | | | | Mean |
|---|---|---|---|---|---|
| | None | Formate | Phthalate | Sulpho-phthalate | |
| 0.5 mole | 460 | 440 | 210 | 400 | 377 |
| 2,5 mole | 625 | 290 | 275 | 310 | 375 |
| Mean | 542 | 360 | 242 | 355 | 376 |

Difference in Extension at Grain Crack Between Naturally Aged and Unaged Leathers

The drop in the extension at grain crack on natural ageing is very small and unimportant from the practical point of view. Nevertheless it is interesting to observe that the type of masking salt makes a significant difference to the amount of deterioration, but this depends on the period at which the fatliquor was applied, see Table X. Less deterioration occurred in unmasked leathers if the fatliquor was applied before the vegetable retannage. This was also the case but to a less marked degree for the phthalate masked leathers. The reverse was the case with the formate masking, and with the sulphophthalate the period at which the fatliquor was added was unimportant.

Table X

Fall in Extension at Grain Crack on Natural Ageing, (mm.)

| Period at which fatliquor offered | Type of Masking Salt | | | | Mean |
|---|---|---|---|---|---|
| | None | Formate | Phthalate | Sulpho-phthalate | |
| before veg. | 0.06 | 0.50 | 0.30 | 0.20 | 0.27 |
| after veg. | 0.46 | -0.50 | 0.50 | 0.25 | 0.18 |
| Mean | 0.26 | 0.00 | 0.40 | 0.22 | 0.22 |

The leathers that had been tanned with the large amount of chromium ave a smaller loss of extension than those that had been tanned with only % Kromex. The average loss of extensibility is 5% Kromex 0.37 mm., )% Kromex 0.08 mm.

Relationship Between Natural and Accelerated Ageing

The object of accelerated ageing is to duplicate the effects of natural ageing in as short a time as possible. Previous work has shown that storage at 50°C and 95+% r.h. for 3 weeks roughly corresponds to about 9 months storage under normal conditions of temperature and humidity when the leathers contain little or no organic acid anions. In the present work it has again been shown this is the case, and the accelerated method of ageing is not applicable when large quantities of organic masking salts are present. The accelerated ageing test shows a deterioration in leathers containing masking salts which does not occur on natural ageing. However, the test is not completely valueless because factors not related to the application of masking salts show the same trend in both types of ageing. For example the amount of chrome tanning salt has the same effect on the deterioration regardless of the method of ageing.

In addition to the two ageing tests given above, samples of the original leather were tested according to the Innes Peroxide test, and were assessed for damage and allotted scores on the scale 0, good leather, little damage, to 4, poor leather, badly damaged. The results of this test correlate strongly (0.1%) with the fall in load at grain crack on accelerated ageing and not quite so strongly (5%) with the fall in load at grain crack on natural ageing, see Table XI.

Table XI
Relationship Between Innes Peroxide Test and Loss of Grain Strength

| Type of masking salt | Drop in load at grain crack (accelerated ageing) | Innes Test Score | Drop in load at grain crack (natural ageing) |
|---|---|---|---|
| None | 690 lb./in. | 2.75 | 540 lb./in. |
| Formate | 590 " " | 2.62 | 360 " " |
| Phthalate | 450 " " | 1.94 | 240 " " |
| Sulphophthalate | 420 " " | 1.75 | 350 " " |
| | r = 0.44 | | r = 0.27 |

Results quoted are means of 8 samples.

## DISCUSSION AND CONCLUSIONS

Apart from the confirmation of our previous findings with regard to the accelerated ageing test, some important observations can be made on the strength and durability of chrome-retan leather. During preliminary work on liming it was discovered that cleaner pelt resulted if skins were limed in a warm lime and obviated the necessity for bating. In this experiment it was found that a warm lime gave stronger leather with a more extensible grain and has no effect on the durability of the leather.

The amount of chrome offered is very important, the high amount of chrome giving much weaker leather than the low amount as determined by both the buckle tear load and load at grain crack. Although the high amount of chrome offered gives the weaker leather, leathers tanned with the large amount deteriorate less than the others.

Whilst masking did not bring about spectacular increases in the strength of the leather, the rate of deterioration was markedly reduced. The protection afforded by the masking salts on warm humid storage, however, was not as great as that under normal storage conditions. Increase in the amount of masking salt did not always increase the degree of protection afforded the leather.

The degree of neutralising had no influence on the strength of the original leather, but un-neutralised leather lost strength and extensibility more rapidly than the neutralised leather.

The period at which the fatliquor was offered was found to be important. In all tests the application of the fatliquor after retanning resulted in stronger and more extensible leather. On the other hand leathers which had received the fatliquor after the chrome tannage but before the vegetable retannage were found to deteriorate less than the others. This may mean that optimum results can be obtained if portion of the fatliquor was added before retannage and the remainder afterwards. This factor will be investigated in a subsequent experiment.

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# R.B. 178. THE USE OF PHOSPHATES IN NEUTRALISING FOR CHROME-RETAN LEATHERS

by

R.L. Sykes and D.A. Williams-Wynn.

## SUMMARY

Previous work has indicated that the loss of strength in chrome retan leather is associated with the moisture content of the leather, thus indicating that chemical changes take place on storage. Working from this premise it was thought that inactivation of the chrome tanning salts present in leather prior to retanning may produce a stronger product. Phosphates, which are known to displace sulphate from chromium complexes were used in the present work; three commercially available materials were compared (Calgon, Vitrafos and Phosphate Glass 696). A number of other factors were also varied in the experiment, viz. basicity of chrome tannage, degree of retannage and drying methods.

Various physical tests were carried out on the leathers, details of which are given in the report, and whilst each test measures different components of the over-all strength of a leather it would appear that, in general, strength is reduced by the use of a high basicity chrome tannage and by larger amounts of vegetable extract. The two phosphates having the smallest molecular size (Calgon and Vitrafos) were particularly useful in improving strength. Increases of 10 - 30% were found compared with control samples. After accelerated ageing these phosphate treated leathers were still stronger than the controls, but the relative improvement was less. An indication is given of other work on this problem which is currently under way.

## INTRODUCTION

Work carried out in the U.S.A. some years ago[1] indicated that retanned chrome leather was significantly weaker than full-chrome eather made from similar quality raw stock. Figures quoted indicate that ıp to 25% reduction in tearing strength may be brought about by retanning, ınd as much as 40% reduction in grain strength. Because retanning plumps p the leather giving few fibres per unit thickness this is obviously a partial xplanation of this reduction in strength. However, since this could account ır only 5 or at the most 10% of the strength loss, other factors have entered into the picture. It is probable that this is in part due to chemical reaction between the vegetable tannin and the chrome tanning salt already in the leather. Dudley[2] has shown that the pH of chrome solutions decreases on ageing in the presence of vegetable tannins. On the other hand, he also found that once the leather had been manufactured there were negligible changes in the pH of its aqueous extract on storage. Nevertheless, vegetable retanned leathers are known to have a tendency towards becoming "tender" with time. Previous work [3] has shown that this is probably only true when the leathers are stored in conditions of high relative humidity which indicates that chemical changes are probably taking place. Liberation of sulphate from chrome tanned leather by vegetable tannins was demonstrated some years ago [4]; a possible line of approach to this problem of preventing deterioration would therefore be to render the chrome leather less reactive chemically. One way of doing this would be to displace sulphate by the more strongly bound phosphate ion prior to retanning with vegetable extract. The other alternative of retanning with inert resins which are deposited within the leather is known to produce leathers having better ageing characteristics; unfortunately the cost of these materials is high which renders them less attractive on economic grounds. The present experiment has as its main function the comparison of various commercially available phosphates as possible agents for modifying chromed stock prior to retanning with vegetable extracts.

## EXPERIMENTAL

### Plan of the Experiment

#### Factors Varied

A Location of pelt in hide

- (1) butt
- a belly

B Basicity of chrome liquor used

- (1) 33% basic
- b 50% basic

CD Type and amount of phosphate used

- (1) none )
- c 2% Calgon )
- d 2% Vitrafos ) on blue shaved weight.
- cd 2% '696' )

E Amount of extract offered during retannage

(1) 2% powdered mimosa
e 15% powdered mimosa

F Method of drying

(1) paste drying
f toggling

Preparation of the Leathers

Two wet-salted hides were washed in running water for 1 hour, paste unhaired in a drum containing 1% $Na_2S$, 5% water and 2% lime for ½ hour, washed and put into a straight lime liquor for 3 days. The hides were cut and numbered and then sorted for chrome tannage. The samples for 33% basic tannage were completely delimed with ammonium chloride at 37°C, and pickled in 90% water, 5% salt and 1% sulphuric acid for 1 hour. 8% Kromex chrome tanning salt was dissolved in 10% water and added to the pickle in 3 portions at ½ hour intervals. The pieces were drummed for 4 hours then left in drum overnight. Next day the pH was adjusted from 3.4 to 3.7 with bicarbonate.

The samples for 50% basic tannage were 5/8 delimed with ammonium chloride at 37°C, pickled in 60% water, 5% salt and 1-1/8% sulphuric acid for 15 min. then 8% "Kromex" chrome tanning salt (equivalent to 2% $Cr_2O_3$) previously dissolved in 40% water and basified to 50% basicity with soda ash was added. The pieces were drummed for 4 hours then left in liquor over-night. On the following day the pH was adjusted from 3.5 to 3.7.

After splitting all pieces were washed and sorted for neutralising; those to get phosphate were treated with 2% commercial material in 100% water for 15 min. prior to adding 1% sodium bicarbonate. The control pieces were neutralised with 1% bicarbonate in 100% water. All neutralisings were of ½ h. duration. After neutralising the leather was washed in running water for 10 min. and sorted for retanning.

Retannage was done in drums by adding the powdered extract to the wet leather, either 2% or 15% on shaved leather weight, and drumming until all extract was taken up - 1 hour.

All the pieces were washed in warm water then dyed with 1%

pH of 5% Aqueous Extract

| Original Leather | | 33% basic | | | | | 50% basic | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | nil | calgon | vitrafos | 696 | Mean | nil | calgon | vitrafos | 696 | Mean |
| butt | low retan | 3.96 | 3.90 | 4.18 | 4.15 | 4.05 | 3.88 | 3.90 | 4.03 | 4.22 | 4.01 |
| | high retan | 3.82 | 4.14 | 3.99 | 3.93 | 3.97 | 3.83 | 3.92 | 4.12 | 3.95 | 3.95 |
| belly | low retan | 3.95 | 4.03 | 4.11 | 4.20 | 4.07 | 3.91 | 3.93 | 4.03 | 4.02 | 3.97 |
| | high retan | 3.71 | 3.96 | 4.00 | 4.00 | 3.92 | 3.86 | 3.94 | 4.00 | 3.99 | 3.95 |
| Mean | | 3.86 | 4.01 | 4.07 | 4.07 | 4.00 | 3.87 | 3.92 | 4.04 | 4.04 | 3.97 |

over-all mean 3.98

| Aged Leather | | 33% basic | | | | | 50% basic | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | nil | calgon | vitrafos | 696 | Mean | nil | calgon | vitrafos | 696 | Mean |
| butt | low retan | 3.78 | 3.75 | 3.91 | 3.88 | 3.84 | 3.72 | 3.74 | 3.89 | 3.90 | 3.81 |
| | high retan | 3.66 | 3.71 | 3.84 | 3.82 | 3.76 | 3.64 | 3.72 | 3.86 | 3.88 | 3.77 |
| belly | low retan | 3.79 | 3.77 | 3.86 | 3.99 | 3.85 | 3.74 | 3.78 | 3.90 | 3.91 | 3.83 |
| | high retan | 3.67 | 3.77 | 3.82 | 3.87 | 3.78 | 3.79 | 3.73 | 3.86 | 3.84 | 3.80 |
| Mean | | 3.72 | 3.75 | 3.86 | 3.89 | 3.81 | 3.72 | 3.73 | 3.88 | 3.88 | 3.84 |

over-all mean 3.82

to face page 71.

Nap leather brown (I.C.I.) at 50°C followed after 10 min. with ½% formic acid. Fatliquoring was in two stages. The first was an anionic fatliquor composed of 1½% sulphonated whale oil, 1% mineral oil, 1% whale oil, 0.25% sulphonated fatty alcohol in 100% float at 55°C for ½ h. The second was a topping with ½% cationic fatliquor (Lipamin liquor O - B.A.S.F.). After horsing over-night the leather was sorted for drying, one lot being paste dried using Primal L ("Rohm & Haas) on a "Secotherm" type unit operating at 70°C, the other nailed out.

When dry the leathers were damped back, staked and dried off, after which they were conditioned at 70°F, 65% r.h. before testing. Duplicate samples were cut for lastometer, stitch tear, shrinkage temperature and tongue tear tests, one set being tested immediately. The other set was aged for 4½ months at 40°C, 75% r.h. then reconditioned before final testing.

## RESULTS

### Chemical Analyses

It was impracticable to analyse separately all 128 leathers, so the following procedure was adopted. Factors which were thought to have little effect on the chemical analysis, i.e. the duplicates and the method of drying, were pooled, reducing the number of groups to 32. The leathers in each of these groups were ground in a Wiley mill, the powder thoroughly mixed and conditioned before analysis.

### pH of 5% Aqueous Extract

The ground leather was weighed into a flask and 20 times its weight of distilled water added. The flasks were shaken for 5 h. then stood over-night. The following morning the pH was measured on each, and the values are those given in the table. The only observations that could be drawn from these results were the increase in pH when phosphates were used, more particularly Vitrafos and 696, and the small but definite reduction in pH with ageing. The other factors have no significant effect on the pH.

### Basicity

The basicity of the leather was determined using two methods:-

the A.L.C.A. official method for sulphate basicity and the method for over-all basicity developed by Stubbings & Theis [5].

ALCA Sulphate Basicity

This determination is of little value because all the leathers treated with phosphate had a basicity of 100%; the untreated leathers had a basicity of ca.85%.

Over-all Basicity

This method consisted of extracting leather with potassium oxalate/sulphuric acid buffer and by back-titration measuring the amount of hydroxyl ion attached to the chrome. Results are given below.

Basicity

Original Leather

| | nil | calgon | vitrafos | 696 | Mean |
|---|---|---|---|---|---|
| 33% basic | 66.6 | 50.4 | 52.4 | 53.6 | 55.7 |
| 50% basic | 69.2 | 50.6 | 55.5 | 55.0 | 57.6 |
| Mean | 67.9 | 50.5 | 53.9 | 54.3 | 56.6 |

Aged Leather

| | nil | calgon | vitrafos | 696 | Mean |
|---|---|---|---|---|---|
| 33% basic | 69.9 | 57.3 | 50.5 | 52.9 | 57.6 |
| 50% basic | 69.5 | 57.9 | 55.5 | 57.0 | 60.0 |
| Mean | 69.7 | 57.6 | 53.0 | 54.8 | 58.5 |

Original Leather

| | nil | calgon | vitrafos | 696 | Mean |
|---|---|---|---|---|---|
| 2% wattle | 65.2 | 46.6 | 54.4 | 54.8 | 55.2 |
| 15% wattle | 70.7 | 54.3 | 55.8 | 55.8 | 59.1 |
| Mean | 67.9 | 50.3 | 55.1 | 55.3 | 57.1 |

Aged Leather

| | nil | calgon | vitrafos | 696 | Mean |
|---|---|---|---|---|---|
| 2% wattle | 69.2 | 55.1 | 51.3 | 54.9 | 57.6 |
| 15% wattle | 70.3 | 60.2 | 54.6 | 55.0 | 60.0 |
| Mean | 69.7 | 57.6 | 52.9 | 54.9 | 58.8 |

Although the phosphate treated leathers had a sulphate basicity of ca. 100% compared with ca. 85% for the untreated, the over-all basicity is in fact markedly lower than the untreated. On ageing only the untreated and Calgon treated leathers became more basic, which indicated that acid was being liberated from the complex. In the case of Vitrafos and "696" there was little change in the over-all basicity. The other factors affected the basicity only slightly.

$Cr_2O_3$ and $P_2O_5$ on Hide Substance

The chrome content varied only slightly and the data obtained from this analysis contained no information of interest, the average value being 5.89% on hide substance.

The $P_2O_5$ content of the leathers was determined colorimetrically and gave the following results for the three phosphates used: Calgon 4.8%, Vitrafos 4.3%, "696" 4.7%, all based on hide substance. In view of the differing $P_2O_5$ contents of the phosphates used, these figures are reflections of this rather than varying uptakes. Furthermore the wattle extract used in this work had a small $P_2O_5$ content which will raise the values obtained.

Thickness

The only factors which affected thickness were degree of retannage and method of drying. The following table gives the average values in mm.

| | low retan | high retan | Mean |
|---|---|---|---|
| pasted | 1.17 | 1.33 | 1.25 |
| nailed | 1.25 | 1.41 | 1.33 |
| Mean | 1.21 | 1.37 | 1.29 |

The thickness was not affected by the ageing treatment.

Shrinkage Temperature

Immediately after manufacture all but two of the leathers stood the boil, but after ageing most shrinkage temperatures were appreciably below 100°C. The only factors which had a significant effect were the type of phosphate and the amount of retanning material.

| | nil | calgon | vitrafos | 696 | Mean |
|---|---|---|---|---|---|
| 2% wattle | 90.9 | 84.1 | 86.5 | 85.7 | 86.8 |
| 15% wattle | 88.0 | 85.2 | 85.6 | 84.2 | 85.7 |
| Mean | 89.4 | 84.6 | 86.0 | 84.9 | 86.1 |

The only point of real interest is that when phosphates were used, the shrinkage temperature of aged leather was somewhat lower than that of the controls. The degree of retannage had a surprisingly small effect.

Tongue Tear Loads

A 1 inch slit was made in the leather and the tear carried out in the tensile machine. The factors which affect the tear strength are given below. Loads are in lb./in.

| Basicity of chrome liquor used | original | aged | % of original |
|---|---|---|---|
| 33% basic | 319 | 200 | 64 |
| 50% basic | 279 | 162 | 58 |
| Mean | 299 | 181 | |

Apart from the general reduction in strength due to ageing, and the lower original strength of the leather tanned with 50% basic chrome liquor it will be seen that the latter lost strength more quickly than the leather chromed with 33% basic chromium.

| Type and amount of phosphate used | Original | | Aged | | % of original |
|---|---|---|---|---|---|
| | Strength | % of control | Strength | % of control | |
| none | 249 | - | 176 | - | 71 |
| 2% Calgon | 340 | 136 | 196 | 111 | 58 |
| 2% Vitrafos | 323 | 130 | 194 | 110 | 60 |
| 2% 696 | 284 | 114 | 159 | 90 | 56 |
| Mean | 299 | | 181 | | |

The use of phosphate increased the strength particularly in the case of "Calgon" and "Vitrafos" where improvements of about 1/3 were obtained. The "696" was however less effective. On ageing, the "Calgon" and "Vitrafos" treated leathers were still slightly stronger than the control but the rate of deterioration was apparently greater. The "696" treated leather was in fact weaker than the control after ageing.

| Amount of extract offered during retannage | original | aged | % of original |
|---|---|---|---|
| 2% powdered wattle | 331 | 202 | 61 |
| 15% powdered wattle | 267 | 160 | 60 |
| Mean | 299 | 181 | |

Leathers made with the large amount of wattle extract were much weaker than those made with 2%. This is a fact well known in the leather industry. The most interesting observation from the above table is the fact that the heavily retanned leather did not lose strength at a greater rate than the lightly retanned material.

The other factors did not have a significant effect on the tongue tear load.

<u>Stitch Tear Loads</u>

The stitch tear loads were measured at two positions on the sample at right angles to each other, the mean of these being taken as the tearing load of the leather. All loads are recorded in lb./in.

| Basicity of chrome liquor used | original | aged | % of original |
|---|---|---|---|
| 33% basic | 947 | 837 | 88 |
| 50% basic | 816 | 710 | 87 |
| Mean | 882 | 778 | |

The 50% basic tannage gave leather that was weaker than that obtained from the 33% basic tannage but here the deterioration on ageing was no more rapid, in contrast to the tongue tear loads.

| Type and amount of phosphate used | original | aged | % of original |
|---|---|---|---|
| none | 820 | 754 | 92 |
| 2% Calgon | 1012 | 829 | 82 |
| 2% Vitrafos | 922 | 815 | 88 |
| 2% 696 | 773 | 694 | 90 |
| Mean | 882 | 778 | |

The use of Calgon and Vitrafos greatly increased the strength of retan leather whilst 696 did not make a significant difference, but those leathers that initially were the strongest lost strength at a greater rate than the control, so that after ageing differences between the leathers were much less marked.

| Amount of extract offered during retannage | original | aged | % of original |
|---|---|---|---|
| 2% powdered wattle | 962 | 881 | 91 |
| 15% powdered wattle | 802 | 665 | 83 |
| Mean | 882 | 778 | |

The use of a large amount of extract for retannage caused a substantial reduction in strength. In addition, the heavily retanned leather lost strength more rapidly on ageing than the lightly retanned leather.

None of the other factors approached significance and so had negligible effect on the strength of the leather.

Load at Grain Crack

The load at grain crack can be measured with the lastometer. The values given in the tables below are recorded in lb./in.

| Basicity of chrome liquor used | original | aged | % of original |
|---|---|---|---|
| 33% basic | 1222 | 915 | 75 |
| 50% basic | 994 | 803 | 81 |
| Mean | 1108 | 859 | |

The load needed to crack the grain when 50% basic liquor was used, was much less than that needed to crack leather from 33% basic liquors. The reduction of strength with ageing was however more marked with the 33% basic tanned leathers.

The effect of the degree of retannage depended on the pre-treatment of the leather. This interaction is given in the following table:-

| | original | aged | % of original |
|---|---|---|---|
| 2% wattle nil | 1230 | 895 | 73 |
| 2% wattle 2% Calgon | 1182 | 999 | 85 |
| 2% wattle 2% Vitrafos | 1060 | 905 | 85 |
| 2% wattle 2% 696 | 1157 | 869 | 75 |
| Mean | 1157 | 917 | 80 |
| 15% wattle nil | 746 | 640 | 86 |
| 15% wattle 2% Calgon | 1030 | 748 | 73 |
| 15% wattle 2% Vitrafos | 1231 | 851 | 69 |
| 15% wattle 2% 696 | 1228 | 964 | 79 |
| Mean | 1059 | 801 | 76 |

Phosphate pretreatment had no significant effect on the strength of the grain when only a small amount of wattle extract was used for retanning, but the effect was large and beneficial when the leather was heavily retanned.

In the case of lightly retanned leathers, phosphate, particularly "Calgon" and "696", reduced the rate of loss of grain strength. This was however not the case for the heavy retannages where proportionately the control had retained its strength better than the phosphate treated leathers. Because of their higher initial strength, the phosphate treated leathers were still the stronger after ageing in terms of real strength.

Extension at Grain Crack

The extension as measured on the lastometer is a good indication of the lasting properties of leather. An extension of more than 7.00 mm. means that the leather will be trouble free from the point of view of grain crack. The factors which affected the extensibility are given below. The units used are mm.

| Location of the sample in the hide | original | aged | % of original |
|---|---|---|---|
| butt | 7.58 | 6.95 | 92 |
| belly | 7.99 | 7.15 | 89 |
| Mean | 7.78 | 7.05 | |

As expected the belly areas were more extensible than the butt in both the aged and original leathers both of which had satisfactory extensions.

| Basicity of chrome liquor used | original | aged | % of original |
|---|---|---|---|
| 33% basic | 8.05 | 7.22 | 89 |
| 50% basic | 7.51 | 6.87 | 92 |
| Mean | 7.78 | 7.05 | |

The 50% basic tanned leather was less extensible than the 33% basic tanned leather. Both however, were affected to a similar extent by ageing.

| Amount of extract offered during retannage | original | aged | % of original |
|---|---|---|---|
| 2% powdered wattle<br>15% powdered wattle | 7.90<br>7.65 | 7.20<br>6.90 | 91<br>90 |
| Mean | 7.78 | 7.05 | |

Heavily retanned leather was less extensible than lightly retanned leather, but the interesting observation was the fact that it did not deteriorate any more rapidly.

| Method of drying | original | aged | % of original |
|---|---|---|---|
| paste drying<br>nailing | 7.56<br>8.01 | 6.86<br>7.24 | 91<br>90 |
| Mean | 7.78 | 7.05 | |

As expected paste drying gave leather that was less extensible than that which had been nailed, but ageing affected the extensibility of both types equally.

## DISCUSSION OF RESULTS

Before considering in detail the effect which the various phosphates had on chrome retan leather, some points of more general interest which are applicable to chrome-retan leather will be mentioned.

Firstly, it seems to be quite conclusive that the basicity of the chrome tanning salt affects the properties of the finished leather. In full-chrome leather certain advantages associated with the use of a short pickle/ 50% basic process have been conclusively demonstrated(6). The present results serve to emphasise the necessity of not retanning some poor chrome stock as a last resort but that quite major changes in processing may be necessary if satisfactory retan leather is to be made.

All the leather used in this experiment was split in the blue state, differences in final thickness were therefore due to retanning and drying techniques. Whilst actual strengths of individual pieces of leather may vary because of thickness changes, it is found that thickness variations have a negligible effect on the strength of the leather compared with those due to process changes.

The use of phosphate materials appear to make possible the manufacture of retan leathers of satisfactory strength. Two of three commercially available phosphates gave on the average significantly stronger leathers; these were "Calgon" and "Vitrafos". The other product, "Phosphate glass 696" was less effective, and it is interesting to note that "696" has much larger molecular size than the other two products. Recent work carried out in England [7] also indicated that no marked improvement in the strength of chrome-retan leather was found when "696" was used as an auxiliary.

Of equal importance to the original strength of leather is the ability to retain strength on storage. A previous experiment [3] had indicated that chrome-retan leather was likely to deteriorate under warm, humid conditions much more rapidly than under dry conditions. The conditions used in this experiment were roughly equivalent to 12 - 18 months normal storage.

The figures which have been quoted in the text indicate that in the majority of cases the actual strength of the aged phosphate treated leathers was still greater than that of the controls. Relatively the improvement imparted by these auxiliaries was less pronounced than it was immediately after manufacture. For this reason the present experiment cannot be considered to have been completely successful. However, information on the general problem of retanning has been obtained which should be of value to tanners. Also in the light of the experience gained from the present experiment, further work is being undertaken to follow up the findings on basicity of tannage, to determine whether there is a limiting value for fall-off in strength with increasing amounts of retannage, and finally to investigate the possibility of finding more rapid methods of testing the storage stability of chrome retan leather.

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# R.B. 187. CHROME RETAN LEATHER : THE EFFECT OF COMPLEXING MATERIALS USED IN NEUTRALISING

by

D.A. Williams-Wynn.

## SUMMARY

A preliminary experiment showed that variations of three factors in the manufacture of chrome retan leather, viz. type of liming, type of chrome tannage, and duration of vegetable retannage gave differences of about 50% in the strength of these leathers.

The use of masking agents in the chrome tannage or complexing materials in neutralising had not reduced the rate of deterioration of the leather on storage but the use of the latter materials had resulted in a considerable increase in the initial strength of the leather.

## INTRODUCTION

Results from previous experiments have indicated that acidity plays some part in the tendering of chrome-retan leather on storage [(1)]. Buckle tear loads and pH both fall on ageing and since it is thought that the production of acid causes both these effects, attempts were made to replace the sulphate groups from the chrome-collagen complex with materials that are more strongly combined. For example, various poly-phosphates were tried as neutralising auxiliaries, and small amounts of formate were used as masking agents during tannage. At the level of masking tried, little effect was observed as regards pH stability [(1)], and the phosphate treated leather, whilst initially stronger, deteriorated as rapidly as the control leathers [(2)]. However, this initial work showed that various factors play a most important role in improving the initial strength of the leather. Three of these factors were associated in one tannage of a number of sides of matched pairs, the other sides being tanned by methods which are expected to produce weak leather. Details of the preliminary experiment are as follows:-

## PRELIMINARY EXPERIMENT

Treatments Varied

| | Good Tannage | Poor Tannage |
|---|---|---|
| Liming | 4 day paddle lime | 1 day drum lime |
| Tannage | $7\frac{1}{2}$% chrome salt<br>33% basic | $7\frac{1}{2}$% chrome salt<br>50% basic |
| Retannage | 15% wattle extract<br>1 hour | 15% wattle extract<br>6 hours |

All other treatments in the tannage were identical for the 2 sets of skin.

The following are the results of determinations of buckle tear strength and lastometer extension at grain crack.

| | Good Tannage | | | Poor Tannage | | |
|---|---|---|---|---|---|---|
| | original | aged 6 wk | % loss | original | aged 6 wk | % loss |
| B.T. strength lb./in. | 865 | 529 | 37.5 | 574 | 344 | 39.5 |
| Lastometer extension mm. | 7.88 | 5.21 | 34.0 | 7.02 | 4.72 | 33.0 |

The above results show how dependent the strength of the leather is on the summed effects of the changes in tannage, which if made singly, bring about much smaller variations in strength.

## PLAN OF THE MAIN EXPERIMENT

In view of the surprisingly small effect of masking, found in a previous experiment [(1)], it was decided to examine this factor further in the present experiment. In addition, to try to reduce the sulphate present, a comparison was made between formic and sulphuric acids for pickling. Calgon, the most effective of the phosphates tried in the previous experiment [(2)], was again used in the neutralising but in increased amounts, and was compared with citrate and oxalate, two materials which form stable complexes with chromium and should make the chrome leather more inert to the action of vegetable tannins. Normal neutralising was also compared with an excessive amount.

Since the duration of retannage has on several occasions been shown to affect the strength, a factor was included to determine whether it is essential that retanned leather be dried immediately after retannage or whether the loss in strength is associated only with prolonged drumming. The experiment was arranged as a $\frac{1}{4}$ replicate of a $2^8$ factorial design, details of which are given below:-

Factors Varied

A Type of pickle acid

- (1) sulphuric acid
- a formic acid

B Masking of chrome tannage

- (1) none
- b $\frac{1}{2}$ mol. formate/mol. $Cr_2O_3$

C Amount of chrome offered

- (1) 1% $Cr_2O_3$
- c 3% $Cr_2O_3$

DE Neutralising materials

- (1) sodium bicarbonate only
- d 3% calgon + $NaHCO_3$
- e 3% Na citrate + $NaHCO_3$
- de 3% Na oxalate + $NaHCO_3$

F Degree of neutralisation

- (1) 1% sodium bicarbonate $\frac{1}{2}$ h.
- f 3% sodium bicarbonate 1 h.

G Amount of wattle extract offered

- (1) 5% wattle extract
- g 15% wattle extract

H Time in pile damp before drying

- (1) none
- h 3 days.

Details of Tannages

A dried light hide was soaked for 3 days, drum unhaired, then limed in a flat lime for 3 days. After scudding and fleshing, 128 pieces were cut out in 8 blocks of 16 samples and numbered. All the pieces were given a thorough deliming with 2% $NH_4Cl$ for 1 h. at 35°C in a 250% float.

The delimed pieces were sorted into two groups according to factor A (type of pickle acid) and were given either 0.75% sulphuric acid or 0.25% sulphuric acid and 0.5% formic acid in a 100% float of 7.5% salt solution for 1 h.

The pickle liquor was drained and the pickled pieces sorted for factors B and C (type and amount of chrome tannage). Samples were tanned in small glass drums in a 100% float of 5% salt solution to which the chrome liquor was added. The final volume was made up to 150% float. Tanning took 24 h., then the pH was raised slowly to 3.8 with sodium bicarbonate. After washing, the pieces were horsed up for 48 h.

The pieces in the blue were sorted for DE (type of neutralising material) and drummed in 100% float of solutions containing 3% of the requisite additives or water for 5 min. 1% sodium bicarbonate was then added and drummed a further 20 min. Half the liquor was drained off and half the pieces removed as determined by factor F (degree of neutralisation). The remainder obtained a further 2% sodium bicarbonate for 30 min. All pieces were washed thoroughly in running water for 20 min.

The neutralised pieces were sorted for factor G (amount of wattle extract) and the requisite quantities of extract given in a 100% float. After retanning for 1 h. the pieces were fatliquored with 3.5% anionic fatliquor followed after 15 min. with 0.5% cationic topping.

Drying was commenced immediately after setting out and sorting for factor H (time in pile before drying), one lot being pasted on a Secotherm unit, the remainder wrapped in polythene sheeting and kept damp for 3 days before drying under the same conditions.

## RESULTS

### Assessments of the Leathers

#### Buckle Tear Load

The leathers were tested soon after manufacture and then after three and six weeks accelerated ageing, (95+ % r.h., 50°C). The original leather was reasonably good, having an average buckle tear load of 788 lb./in. Confirming the work done previously [2], the Calgon treated eathers were stronger than the control, particularly when 3%

$Cr_2O_3$ was used, but more important is the bigger increase in strength with citrate and oxalate, see Table I.

Table I
Buckle Tear Load, (lb./in.)

| Amount of chrome offered | Neutralising Materials | | | | Mean |
|---|---|---|---|---|---|
| | sodium bicarbonate | Calgon + $NaHCO_3$ | Na citrate + $NaHCO_3$ | Na oxalate + $NaHCO_3$ | |
| 1% $Cr_2O_3$ | 777.5 | 791.3 | 806.3 | 856.2 | 807.8 |
| 3% $Cr_2O_3$ | 656.3 | 747.5 | 841.9 | 828.1 | 768.4 |
| Mean | 716.9 | 769.4 | 824.1 | 837.1 | 788.1 |

As expected, the large amount of chrome offered gave much weaker leather in the control pieces, but the effect of the chrome was reduced when phosphate, citrate or oxalate was used in neutralising.

The amount of wattle extract offered also made a significant difference, although the difference in strength between the leathers tanned with the different amounts was not as large as expected. An interaction of low significance was found between the amount of wattle and the amount of chrome offered and is shown in Table II.

Table II
Buckle Tear Load, (lb./in.)

| Amount of chrome offered | Wattle Extract | | Mean |
|---|---|---|---|
| | 5% extract | 15% extract | |
| 1% $Cr_2O_3$ | 822.2 | 793.4 | 807.8 |
| 3% $Cr_2O_3$ | 789.1 | 747.8 | 768.4 |
| Mean | 805.6 | 770.6 | 788.1 |

The storage time between retanning and drying had a quite nsignificant effect, so the reduction in strength for the prolonged retanning iven in previous experiments may be due to the mechanical action in the etanning drum, causing more intimate reaction of the wattle tannin with the hrome pelt.

The difference in buckle tear load was determined after ageing for three weeks and six weeks at elevated temperature and humidity. The average reduction in buckle tear load after the first ageing period was 71 lb./in. and the average after the second period 148 lb./in. Some factors changed the rate at which the leathers deteriorated, the most important being the amount of vegetable tannin offered. Whereas the original strength of the pieces retanned with 15% wattle extract was 95.5% of the strength of those which obtained 5% wattle, after three weeks ageing they were 89.9%, and after six weeks ageing only 82.0%. This change in strength is given in Table III.

Table III
Buckle Tear Load, (lb./in.)

| Amount wattle extract | Original | Aged 3 wks | Aged 6 wks |
|---|---|---|---|
| 5% wattle | 806 | 756 | 704 |
| 15% wattle | 771 | 679 | 576 |
| Mean | 788 | 717 | 640 |

The only other factor that gave a significant difference in the rate of deterioration was the type of neutralising material used. This shows that when strongly complexing materials were used in neutralising, the rate of deterioration was greater, although in the case of citrate and oxalate the leather was materially stronger than the control even after six weeks accelerated ageing, see Table IV. No other factors influenced the strength or rate of deterioration of the leathers.

Table IV
Buckle Tear Load, (lb./in.)

| Neutralising material | Original | Aged 3 wks | Aged 6 wks |
|---|---|---|---|
| $NaHCO_3$ | 717 | 657 | 596 |
| Calgon + $NaHCO_3$ | 769 | 686 | 615 |
| Citrate + $NaHCO_3$ | 824 | 756 | 657 |
| Oxalate + $NaHCO_3$ | 837 | 758 | 683 |
| Mean | 788 | 717 | 640 |

pH of Aqueous Extract

In previous experiments a relationship between pH of aqueous extract and strength has been shown to exist[(1)], the higher the pH the stronger the leather. In this experiment the trend is again encountered with one notable exception: the degree of neutralisation had no significant effect on the strength of the leather within the limits tested in this experiment, but the pH of the aqueous extract was much higher for the high level of neutralising. The following factors made a significant difference to the pH of aqueous extract.

Amount of chrome offered

1% $Cr_2O_3$, pH 4.53
3% $Cr_2O_3$, pH 4.05

Amount of wattle extract offered

5% wattle extract, pH 4.39
15% wattle extract, pH 4.19

Neutralising materials used

| | |
|---|---|
| Sodium bicarbonate only, | pH 4.01 |
| Calgon + $NaHCO_3$, | pH 4.25 |
| Sod. citrate + $NaHCO_3$, | pH 4.32 |
| Sod. oxalate + $NaHCO_3$, | pH 4.59 |

Degree of neutralisation

| | |
|---|---|
| 1% sodium bicarbonate, | pH 4.01 |
| 3% sodium bicarbonate, | pH 4.57 |

On ageing, the relationship between pH of aqueous extract and strength no longer holds good. In the case of the degree of retannage, the leathers retanned with 15% wattle extract deteriorated more quickly than those which obtained only 5% wattle extract, but this was not associated with an accelerated drop in pH, although in terms of hydrogen ion concentration the increase in acidity may be significant. Thus the change in pH on ageing was 0.2 in each case, but the difference in hydrogen ion concentration was $2.3 \times 10^{-5}$ and $5.2 \times 10^{-5}$ for low and high retanned leathers respectively.

The type of neutralising material affected the change in pH, Calgon, citrate and oxalate reducing the amount that the pH fell compared with the control. Since the original pH of aqueous extract was higher in the case of the leathers which received the additives in the neutralising, the change in hydrogen ion concentration was much less than that of the control, yet the deterioration as determined by strength measurements was greater. Hence it must be concluded that the loss in strength was not entirely due to liberated acid, see Table V, although when the system contained weak acids the effect of the unionised acid must not be overlooked.

Table V

Change in $[H^+]$ and strength after ageing

| Neutralising material | Increase in $[H^+]$ | Loss in strength (lb./in.) |
|---|---|---|
| Sodium bicarbonate | $5.90 \times 10^{-5}$ | 121 |
| Calgon + $NaHCO_3$ | $3.29 \times 10^{-5}$ | 154 |
| Citrate + $NaHCO_3$ | $1.30 \times 10^{-5}$ | 167 |
| Oxalate + $NaHCO_3$ | $1.96 \times 10^{-5}$ | 154 |

## CONCLUSIONS

The preliminary experiment has shown that results from previous factorial experiments give accurate indications of trends which can be translated to large scale work. Three factors, viz., timing, type of chrome tannage, and duration of vegetable retannage are important in determining the strength of chrome-retan leather, since differences of about 50% were obtained. These factors do not affect the tendency for chrome-retan leather to deteriorate.

Attempts at reducing or eliminating the deterioration of chrome retan leather on storage by modifying the chrome tannage or the chrome leather before retannage have not been successful. Although the initial strength was considerably increased by the use of additives in the neutralising, deterioration also increased. This deterioration was associated with an increase in the acidity of the aqueous extract of the leather but was not proportional to the hydrogen ion concentration.

Use of large amounts of retanning material gives low strength leather which deteriorates more rapidly than lightly retanned leather, bearing out the findings of a previous experiment[1].

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# R.B. 190. CHROME RETAN LEATHER : FURTHER STUDIES IN NEUTRALISING AND BLENDING WATTLE WITH SULPHITE CELLULOSE

by

R.L. Sykes and D.A. Williams-Wynn.

## SUMMARY

A further experiment has been completed in which various factors relevant to the manufacture of chrome-retan leather have been studied. The use of blends of wattle and sulphite cellulose extracts were found to produce a leather with improved grain quality, but reduced strength and a tendency to deteriorate more rapidly than when wattle was used alone. The use of a neutral syntan immediately prior to retanning was found to give some improvement in strength when the leather was retanned with wattle. Various complexing salts were also used to neutralise the leather and there was a strong indication that the use of sulphophthalate gives a leather of improved storage stability.

## INTRODUCTION

The use of various complexing salts as components of the neutralising alkali in manufacturing chrome retan leather has already been reported[1,2]. However, in view of the low cost of calcium formate the Institute was asked to study the use of this product; this has been compared with oxalate, the best of the complexing agents previously used, and with sulphophthalate, a product which has been claimed to produce stable chrome complexes. The use of neutralised synthetic tannins is recommended by a number of manufacturers for neutralising chrome leather prior to retannage, hence the use of such an intermediate has also been studied. In all previous experiments undertaken at the Leather Institute, only standard wattle tannin had been used for retanning. It was therefore decided to compare the effects of sulphiting wattle and blending it with sulphite cellulose extracts. Two variations in beamhouse processes were also included. The time in lime after rapid paste unhairing was investigated since this has been found to be of some importance by Australian workers[3]. The use of ammonium salts, particularly chloride, has on occasion been associated with loose grained leather, hence ammonium chloride and sulphate were compared as deliming materials; in addition, the same anion was used in the pickle so that one single anion tannage (sulphate) was compared with one in which the anion was mixed chloride/sulphate[4]. These factors were therefore all included in a $2^7$ factorial experiment, details of which are given below:-

## EXPERIMENTAL

### Factors Varied

A Time in white lime after unhairing

- (1) 2 days
- a 4 days

B Type of anion in deliming (ammonium salt) and pickle

- (1) Sulphate
- b Chloride

CD Neutralising Agents

- (1) 1½% Sodium bicarbonate
- c 3/4% Sodium bicarbonate + 2% Calcium formate
- d 3/4% Sodium bicarbonate + 2% Sodium oxalate
- cd 3/4% Sodium bicarbonate + 2% Sulphophthalate (Implenal UR - B.A.S.F.)

E Pre-retanning Treatment

- (1) Nil
- e 2% Tanigan Extra Special P 1

FG Retanning Material

- (1) 15% Wattle Extract
- f 15% Wattle Extract previously treated with 2½% bisulphite on extract weight
- g 15% Wattle/Tolanin 1 : 1 blend
- fg 15% Wattle/Wargotan 1 : 1 blend.

### Details of Tannages

A 60 lb. wet salted hide was cut into quarters, two of which were soaked, paste unhaired in the drum [5] and placed in flat lime for 4 days. The other two quarters were soaked out two days after the others, unhaired and left in flat lime for 2 days. At this stage the hide was split and the grain splits were cut into pieces approximately 6" × 7" and sorted for factor B (deliming), either 2% ammonium chloride or 3% ammonium sulphate was used. Addition of 3/8% sulphuric acid was made to complete the deliming with ammonium sulphate. When deliming was complete the spent liquor was drained off, the pelts washed in warm water and a pickle made up of either 16% glaubers salt ($Na_2SO_4.10H_2O$) and 3/4% sulphuric acid or 6% common salt (NaCl) and 2.4% commercial hydrochloric acid. The amounts were calculated to give equimolar salt and acid concentrations; 2 h. after pickling commenced, 7% of commercial 33%basic 25%$Cr_2O_3$ content chrome tanning salts (Kromex) was added. Equilibrium pH of the liquors after 24 h. intermittant drumming was 3.8 for the sulphate pickled stock and 3.6 for the chloride pickled stock. At this stage the leather was piled for 3 days, wrung out and sorted into the four lots for neutralising. Samples were neutralised for 3/4 h. in drums, after which the leathers were sorted into eight lots. Those which were not to have the intermediate syntan treatment were retanned for 2 h. with the requisite amount of extract in a 150% float at room temperature. The others were floated in 150% water to which 2% of Tanigan Extra Special P 1 was added and drummed for 15 min. before the extract was added. After retanning all leathers were given a wash in warm water to bring them up to dyeing temperature (55$^{o}$C). They were dyed with 1% Acid Orange which was not exhausted, and the leather was then fat-liquored with 3½% anionic fatliquor, followed by ½% cationic topping. The leather was set out and immediately paste dried. The dry leather was sawdusted prior to hand staking, aired off and then conditioned at 70$^{o}$F and 65% r.h. The leathers were assessed visually for grain condition, and samples were taken for physical testing and ageing test.

## RESULTS

### Evaluation of the Leathers

#### Visual Assessment

Dyeing was noted to be uniform throughout but some differences in tightness of grain or tendency to pipiness were noted. The leathers were therefore sorted into four groups according to the quality of the grain; leather with the best grain was given a score of 0 and those with the worst grain a score of 3. High scores are therefore associated with poor grain. The length of time in lime was found to have quite a marked effect. Total score for the 32 pieces given each liming was:-

| | |
|---|---|
| 2 days in straight lime | 39 |
| 4 days in straight lime | 57 |

indicating that the shorter time is conducive to better grain appearance. A two-way table showing the interaction between neutralising and the retanning blend showed up some significant differences.

| | Neutralising Materials | | | | |
|---|---|---|---|---|---|
| Retanning material | $NaHCO_3$ | $NaHCO_3$ + Formate | $NaHCO_3$ + Oxalate | $NaHCO_3$ + Sulpho-phthalate | Mean |
| Wattle | 7 | 9 | 6 | 7 | 7 |
| Bisulphited wattle | 6 | 8 | 9 | 9 | 8 |
| 1:1 Wattle/Totanin | 2 | 3 | 7 | 4 | 4 |
| 1:1 Wattle/Wargotan | 5 | 7 | 3 | 4 | 5 |
| Mean | 5 | 7 | 6 | 6 | 6 |

The numbers refer to the totals for 4 pieces and if all had the worst grain the maximum number would be 12. It is readily apparent that the wattle/sulphite cellulose blends give a much superior grain, the ammonia neutralised type Totanin being slightly better than the calcium neutralised Wargotan. There was a tendency for the buffer salts to reduce grain quality, the formate being the worst in this respect.

## Buckle Tear Strength

Very few of the factors studied were found significantly to affect the buckle-tear strength of the leather. Of particular interest, however, was the fact that the use of sulphite cellulose products, which gave a better appearance to the leather, were also responsible for reducing the buckle tear strength. An interaction of these factors with the use of the syntan is given in the next two-way table. Figures quoted are means expressed in lb./in.

| | Type of Retannage | | | | |
|---|---|---|---|---|---|
| Pre-retan assist | Wattle | Sulphited Wattle | Wattle/ Totanin | Wattle/ Wargotan | Mean |
| Nil | 792 | 862 | 756 | 835 | 811 |
| 2% Tanigan Extra Special P 1 | 921 | 810 | 772 | 782 | 821 |
| Mean | 856 | 836 | 764 | 808 | 816 |

Statistical analysis of these results shows that the use of sulphite cellulose extract gives a generally weaker leather. The effect of the syntan is confined to its use in conjunction with normal wattle where it brings about a very marked improvement. This finding seems to be well worth following up in future experiments. The various changes in neutralising procedure brought about only trends towards increased strength, not significant improvements as had been found in previous experiments. After ageing for 6 weeks at 95+% r.h. and 50°C the leathers were again tested for buckle tear strength and the loss in strength calculated. Here an interaction between neutralising procedure and the type of retannage proved to be significant. Details are given in the following table, the figures being mean loss in buckle tear strength expressed in lb./in.

Loss in Buckle Tear Strength on Ageing

| | Neutralising Material | | | | |
|---|---|---|---|---|---|
| Retanning material | $NaHCO_3$ | $NaHCO_3$ + Formate | $NaHCO_3$ + Oxalate | $NaHCO_3$ + Sulpho-phthalate | Mean |
| Wattle | 116 | 229 | 251 | 42 | 159 |
| Sulphited wattle | 117 | 108 | 182 | 198 | 151 |
| Wattle/Totanin | 174 | 163 | 262 | 292 | 223 |
| Wattle/Wargotan | 288 | 99 | 214 | 252 | 213 |
| Mean | 174 | 150 | 227 | 196 | 186 |

The sulphite cellulose blends, it will be observed, are on the average much more prone to rapid deterioration, the percentage losses in strength being -

| | |
|---|---|
| Wattle | 19% |
| Sulphited wattle | 18% |
| Wattle/Totanin | 29% |
| Wattle/Wargotan | 26% |

The very small deterioration of the wattle retanned leather made from chrome stock neutralised with sulphophthalate merits further investigation, although taking all the neutralising treatments together only formate has shown an over-all trend towards reducing deterioration. Oxalate neutralised leather deteriorated most rapidly and this confirms the findings of an earlier experiment[2]. There was a tendency for the leather made from stock delimed and pickled with sulphate to deteriorate more rapidly than when the chloride anion is present: a mean loss of 238 lb./in. compared with 120 lb./in. for the chloride samples; this difference however becomes insignificant when the syntan (Tanigan Extra Special P 1) was used prior to retanning.

Lastometer Evaluation

The average thickness of these leathers was in the order of 2.75 mm. and their strengths were beyond the capacity of the lastometer. They were therefore tested by the widely used double-fold, and none of them was found to crack. After ageing they had deteriorated somewhat and the strengths had now dropped so that the majority were within the capacity of the instrument. The results for load at grain crack showed that no factors or interactions were significant at the 5% level, which is the value usually accepted as confirmation that an effect is real. The type of neutralising agent used brought about differences which were significant at the 10% level, but these can only be referred to as probable trends.

| Neutralised with | Load at grain crack after ageing |
|---|---|
| Bicarbonate | 1088 lb./in. |
| Bicarbonate + Formate | 1161 lb./in. |
| Bicarbonate + Oxalate | 1221 lb./in. |
| Bicarbonate + Sulphophthalate | 1001 lb./in. |
| Mean | 1118 lb./in. |

These results indicate that the grain strengths of the leathers

# R.B. 212. CHROME RETAN LEATHER : THE USE OF CERTAIN SYNTANS IN BLENDS WITH WATTLE EXTRACT FOR RETANNING - PART 1

by

D.A. Williams-Wynn and R.L. Sykes.

## SUMMARY

An investigation has been made of the effect of mixtures of syntans and wattle tannins for retanning, the syntan being added in blends with the wattle or separately before the vegetable retannage. Other factors included the type and temperature of neutralising, and the pH of retannage.

Variations in retannage were greater than those brought about by neutralising. Strength characteristics were improved by the use of syntan in the retannage, but there appears to be an optimum pH of application for each type of syntan. Moreover, the syntan that gave the best grain strength was not necessarily the one to give maximum tearing strength.

## INTRODUCTION

A thorough investigation of the use of wattle tannins for the production of chrome-retan leather has been made and the results reported[1-4]. It is evident that wattle alone is capable of producing satisfactory, strong chrome-retan leather, but deterioration on ageing is rapid. This deterioration can be reduced if the chrome tanned hide is modified by masking of the chrome tannage [2,3] or by changes in the normal neutralising process[1,4].

Various syntans have been recommended by the manufacturers for blending with vegetable tannins for retanning, and it has been shown [5] that the inclusion of syntans in retanning blends increases the grain strength of chrome-retan leather. The present investigation was carried out to determine the effect of 25% syntan and 75% wattle blends on the properties of chrome retan leather made under various different conditions.

# EXPERIMENTAL

## Plan of the Experiment

### Factors Varied, and Levels of the Factors

The samples were cut from a hide in the blue, split to give about 2 mm. substance and then were neutralised and retanned in various ways, as described below. The factors and their levels were as follows:-

A Temperature of Neutralising Liquor

- (1) 20°C
- a 40°C

BC Neutralising Agent

- (1) 1% $NaHCO_3$ - ½ h.
- b 1% $NH_4.HCO_3$ - ½ h.
- c 1½% Ca formate - ¼ h., ½% $NaHCO_3$ - ¼ h.
- bc 2% Orotan N - ½ h.

D Temperature of Retanning Liquor

- (1) 20°C
- d 40°C

E Retan Addition

- (1) mixture added in 1 lot - run 40 min.
- e 25% of syntan added - run 15 min, add remainder - run 25 min.

$\overline{FG}$ Composition of Retanning Blend (12% offered)

- (1) 25% wattle + 75% wattle
- f 25% Irgatan AG1 + 75% wattle
- g 25% Orotan TV + 75% wattle
- fg 25% Tannigan Extra Special P1 + 75% wattle

H pH of Blend

- (1) pH 3.5
- h pH 5.0

## Statistical Plan

The experiment was arranged as a ½ replicate of $2^8$ factorial, with the 128 samples cut in 8 blocks of 16 samples each to reduce to a minimum errors due to the intrinsic difference between samples from different locations in the hide.

## Selection and Properties of Syntans

The number of synthetic tannins available is very large and there is almost certainly a great deal of duplication between the various manufacturers. Obviously the choice of materials to be used had to be limited in any one experiment and three products, all comparatively low priced, were used. The choice was governed by such considerations as suitability and availability. The three materials used were:-

| | |
|---|---|
| Irgatan AG1 | - manufactured by Geigy |
| Orotan TV | - manufactured by Rohm & Haas |
| Tanigan Extra Special P1 | - manufactured by Bayer. |

The fact that these materials were used does not indicate that they are recommended by LIRI in preference to syntans produced by other manufacturers.

Irgatan AG1 and Orotan TV both have a pH in the region of 3.5, whilst Tanigan E.S.P1 has a pH of 5.2, thus pH's of retannage were chosen to be at these limits. Adjustment for experimental work was by the addition of sodium hydroxide or sulphuric acid.

It has been suggested that buffering capacity of a retanning material is important, and it is known that buffer salts are added to certain proprietary retanning blends. It was with this knowledge in mind that one factor varied in the experiment was the addition of the syntan prior to or at the same time as the wattle extract. The buffering capacity of the syntans used was determined by titration with acid or alkali. In the experiment the amount of syntan offered was calculated at 3% tannins on the blue weight of leather. Since the amount of non-tannin differed this meant that the concentration of total solids varied considerably. Titration curves were run on solutions containing 25% syntan and are recorded in Fig. 1. It will be seen that the Tanigan Extra Special P1 is virtually unbuffered, whilst after making allowance for the difference in total solids concentration, the buffering capacity increases through Irgatan AG1 to Orotan TV which is very highly buffered.

Preparation of the Samples

The samples were cut from a split hide in the blue. They were sorted into eight groups and washed, then neutralised for $\frac{1}{2}$ hour at either $20^{\circ}$ or $40^{\circ}C$ with one of the neutralising agents in accordance with factor $\overline{BC}$. They were then given a thorough wash in running water, drained and sammed. They were retanned in miniature glass drums, the samples having been sorted for factors D, E, F, G, H. The final float was 150%, but those that had the retan addition in two parts received the syntan or $\frac{1}{4}$ of the total amount of wattle in 100% float, the remaining wattle being added in 50% float. The total amount of retanning agent added was 12%. The samples were washed in warm water and fat liquored with a blend of whale oil, sulphated whale oil, and mineral oil, followed by topping with $\frac{1}{2}$% Lipamin Liquor O, then set out and pasted to dry.

## RESULTS

### pH of Exhaust, Neutralising Liquor

The pH values of the spent neutralising liquors were measured to determine the relative efficiency of the eight neutralising processes, and are recorded in Table 1.

Table 1
pH of Spent Neutralising Liquor

| Temp. of neutralising liquor | Neutralising | | | | Mean |
|---|---|---|---|---|---|
| | 1% $NaHCO_3$ | 1% $NH_4HCO_3$ | 1$\frac{1}{2}$% Ca formate $\frac{1}{2}$% $NaHCO_3$ | 2% Orotan N | |
| 20°C | 6.4 | 6.4 | 5.9 | 4.0 | 5.7 |
| 40°C | 6.2 | 5.7 | - | 3.6 | 5.2 |
| Mean | 6.3 | 6.0 | 5.9 | 3.8 | 5.45 |

It will be seen that the pH of the liquors used at the high level of temperature (40°C) are all lower than the pH of the corresponding liquors used at the low temperature. This probably means that the neutralising effect is greater at the high temperature. The most striking difference is in the choice of neutralising agents, the neutralised syntan, Orotan N, giving a much lower pH than the other neutralising agents.

### pH of Spent Retanning Liquor

Although the retannage liquors were initially at either pH 3.5 or 5.0 it was found that this fell during retannage. In other words, stronger acid was liberated from the leather during retannage. This result was not entirely unexpected as there is considerable evidence that retanning materials react with the chromium complex during retannage and liberate strong acid. The two tables given below record the information obtained:-

Table II

pH of Spent Liquor for Retannages Initially at pH 3.5

| Composition of blend | Retanning material added together | | Retanning material offered in 2 additions | | Mean |
|---|---|---|---|---|---|
| | at 20°C | at 40°C | at 20°C | at 40°C | |
| 100% wattle | 3.3 | 3.1 | 3.2 | 3.0 | 3.15 |
| 75% wattle<br>25% Irgatan AG1 | 3.5 | 3.4 | 3.4 | 3.3 | 3.4 |
| 75% wattle<br>25% Orotan TV | 3.3 | 3.3 | 3.5 | 3.3 | 3.35 |
| 75% wattle<br>25% Tanigan Ex.Sp. P 1 | 3.5 | 3.4 | 3.5 | 3.4 | 3.45 |
| Mean | 3.4 | 3.3 | 3.4 | 3.25 | 3.3 |

Table III

pH of Spent Liquor for Retannages Initially at pH 5.0

| Composition of blend | Retanning material added together | | Retanning material offered in 2 additions | | Mean |
|---|---|---|---|---|---|
| | at 20°C | at 40°C | at 20°C | at 40°C | |
| 100% wattle | 4.2 | 3.9 | 4.45 | 4.0 | 4.15 |
| 75% wattle +<br>25% Irgatan AG1 | 4.55 | 4.4 | - | 4.5 | 4.5 |
| 75% wattle +<br>25% Orotan TV | 4.5 | 4.2 | 4.6 | 4.35 | 4.35 |
| 75% wattle +<br>25% Tanigan Ex.Sp. P 1 | 4.3 | 4.1 | 4.8 | 4.3 | 4.4 |
| Mean | 4.4 | 4.15 | 4.6 | 4.3 | 4.35 |

A high temperature of retannage appears to favour liberation of acid during retannage and in all cases more acid was liberated when 100% wattle was used for retanning; rather surprisingly the most highly buffered syntan - "Orotan TV" showed the next largest change in pH of the spent liquor.

Weight Yields

The weight of the dry leather expressed as a percentage of the blue weight was determined in each case. This is an indication of the amount of retanning material taken up. The high temperature of retanning resulted in a higher weight yield (61.2%) compared with the yield (60.0%) from the low temperature of retanning. The composition of the retanning blend also affected the quantity of material taken up, but the amount taken up from each blend was dependent on pH, see Table IV.

Table IV
Weight Yields, %

| pH of blend | Composition of retanning blend | | | | Mean |
|---|---|---|---|---|---|
| | Wattle only | Irgatan AG1 wattle | Orotan TV wattle | Tanigan Ex.Sp.P1 wattle | |
| pH 3.5 | 59.6 | 61.1 | 61.8 | 60.3 | 60.7 |
| pH 5.0 | 59.8 | 58.6 | 62.3 | 61.4 | 60.5 |
| Mean | 59.7 | 59.8 | 62.1 | 60.9 | 60.6 |

It will be seen that in general the weight yield was increased when syntan forms part of the retanning blend and this increase was greater at the high pH. A notable exception occurred in the blend containing Irgatan AG1 which showed a considerably reduced yield at the high pH.

Thickness

Thickness was computed as a percentage of the thickness of the blue leather before neutralising and retannage. Only two factors were shown to have a really significant effect on the plumping action: the composition of the retanning blend, and the temperature at which retanning was effected. The presence of syntan in the retanning mixture resulted in thinner leather than leather produced from an all wattle retannage, the figures for the four retanning materials being: wattle only 115.6%, Irgatan AG1 + wattle 112.6%, Orotan TV + wattle 108.9%, and Tanigan Extra Special P1 + wattle 112.4%.

The high temperature of retanning, i.e. 40°C, resulted in a thicker leather (114.6%) compared with leather retanned at 20°C (110.2%).

Comparing thickness with weight yield it is seen that the retanning blend which was taken up to the greatest extent did not give the thickest leather. In fact, retannage with the Orotan TV + wattle blend, which gave the greatest weight yield, yielded the thinnest leather, and that which was offered only wattle gave the thickest leather, while the weight yield was least.

Shrinkage Temperature

Shrinkage temperatures were all in excess of 100°C so the determination of the Ts was made in liquid paraffin[6]. The composition of the retanning blend was the only factor to affect the Ts. The presence of syntan slightly increased the Ts, but an interaction between the composition of the retanning mixture and the manner in which it was offered was highly significant, see Table V.

Table V
Shrinkage Temperatures

| Retan addition | Composition of the retanning blend | | | | Mean |
|---|---|---|---|---|---|
| | Wattle only | Irgatan AG1 Wattle | Orotan TV Wattle | Tanigan Ex.Sp.P1 Wattle | |
| 1 lot-40 min. | 120.2 | 124.7 | 124.1 | 125.8 | 123.7 |
| 25% - 15 min. 75% - 25 min. | 123.9 | 123.2 | 123.0 | 123.3 | 123.4 |
| Mean | 122.0 | 124.0 | 123.6 | 124.6 | 123.5 |

When syntans were included in the retanning blend, higher shrinkage temperatures were obtained when the syntan was added in admixture with the wattle than when the syntan was added first, followed, after 15 min. by the wattle extract. The Ts of the leather retanned with wattle only was found to be higher when 25% of the retanning material was added first followed by the remainder, than when the wattle extract was added in one lot.

Buckle Tear Strength

The buckle tear load was determined in the usual way. In this experiment only the composition of the retanning blend exerted considerable influence on the strength of the leather. The strength was increased if the retanning blend contained syntan, but the extent of the increase was influenced by the pH at which retannage was effected, see Table VI. The strength of the leather retanned with only wattle or with Tanigan Extra Special P1 + wattle was unaffected by the pH of the retanning mixture; Irgatan AG1 + wattle mixture gave the strongest leather at pH 3.5, and Orotan TV + wattle the strongest at pH 5.0. It is very likely that these differences are dependent on the composition of the syntan and reference should be made to the titration curves given previously.

Table VI
Buckle Tear Load, (lb./in.)

| pH of blend | Composition of retanning blend | | | | Mean |
|---|---|---|---|---|---|
| | Wattle only | Irgatan AG1 wattle | Orotan TV wattle | Tanigan Ex.Sp.P1 wattle | |
| pH 3.5 | 472 | 621 | 584 | 551 | 551 |
| pH 5.0 | 487 | 541 | 634 | 532 | 548 |
| Mean | 479 | 581 | 609 | 541 | 553 |

Load at Grain Crack

The load at grain crack was measured in the usual way using a lastometer. The composition of the retanning mixture influenced the strength of the grain, the presence of the syntan in the mixture resulting in increased grain strength. The effect of the retanning was however dependent on the pH and this is illustrated in Table VII.

Table VII
Load at Grain Crack (lb./in.)

| pH of blend | Composition of retanning blend | | | | Mean |
|---|---|---|---|---|---|
| | Wattle only | Irgatan AG1 Wattle | Orotan TV Wattle | Tanigan Ex.Sp. P1 Wattle | |
| pH 3.5 | 829 | 1001 | 1039 | 1013 | 970 |
| pH 5.0 | 963 | 941 | 961 | 1014 | 970 |
| Mean | 896 | 971 | 1001 | 1013 | 970 |

When only wattle was used as the retanning material retannage at the higher pH (pH 5.0) yielded strong leather. In the case of the blends of wattle with Irgatan AG1 and Orotan TV stronger leather was produced at the low pH, and in the case of Tanigan Extra Special P1 + wattle, pH had no effect on the grain crack.

The influence of the composition of the retanning mixture on load at grain crack was also dependent on the manner in which the retanning material was added, see Table VIII.

Table VIII
Load at Grain Crack, (lb./in.)

| Retan addition | Composition of retanning blend | | | | Mean |
|---|---|---|---|---|---|
| | Wattle only | Irgatan AG1 Wattle | Orotan TV Wattle | Tanigan Ex.Sp.P1 Wattle | |
| 1 lot - 40 min. | 872 | 944 | 972 | 955 | 936 |
| 25% - 15 min<br>75% - 25 min | 920 | 999 | 1028 | 1072 | 1005 |
| Mean | 896 | 971 | 1000 | 1013 | 970 |

In general leather with the strongest grain was produced from the process in which 25% of the retanning material was given first, followed by the remainder; this is especially true when Tanigan Extra Special P 1 was used.

The high temperature of retanning reduced the load at grain crack; values of 1021 lb./in. and 919 lb./in. were found for temperatures of retanning of 20°C and 40°C respectively.

Extension at Grain Crack

The extension at grain crack was lower for samples retanned at the high temperature. Extensions of 6.44 mm. and 6.73 mm. were found for samples retanned at 40°C and 20°C respectively. More extensible leather was produced when syntan was included in the retanning blend. Extensions obtained were: wattle only 6.29 mm., Irgatan AG1 + wattle 6.58 mm., Orotan TV + wattle 6.86 mm., and Tanigan Extra Special P1 + wattle 6.62 mm.

Dyeing Characteristics

The dyed leathers were assessed for levelness of dye uptake and were allotted scores ranging from 0 for very unlevel dyeing to 5 for good, even dyeing. The neutralising agent was found to have a considerable effect on the levelness of dyeing, the use of Tamol N resulting in a very much more level dye uptake, particularly in the case of the 100% wattle retannage. Details are given in Table IX.

Table IX

Interaction of Neutralising and Retanning on Levelness of Dyeing
(high scores indicate level dyeing)

| Composition of Retanning blend | Neutralising Treatment | | | | Mean |
|---|---|---|---|---|---|
| | $NaHCO_3$ | $NH_4HCO_3$ | Formate + $NaHCO_3$ | Orotan N | |
| 100% wattle | 1.50 | 1.62 | 2.25 | 4.12 | 2.37 |
| 75% wattle + 25% Irgatan AG1 | 1.37 | 1.12 | 1.00 | 3.37 | 1.71 |
| 75% wattle + 25% Orotan TV | 1.75 | 1.50 | 0.87 | 3.12 | 1.81 |
| 75% wattle + 25% Tanigan Ex.Sp.P1 | 1.50 | 1.75 | 2.50 | 3.89 | 2.41 |
| Mean | 1.53 | 1.50 | 1.65 | 3.62 | 2.07 |

It appears that the manufacturers' claim that Orotan N improves dyeing characteristics is fully justified. The composition of the retanning blend also affected the levelness of dyeing and was dependent to some extent on the pH of the retanning liquor. The average values are given in the two way table, Table X.

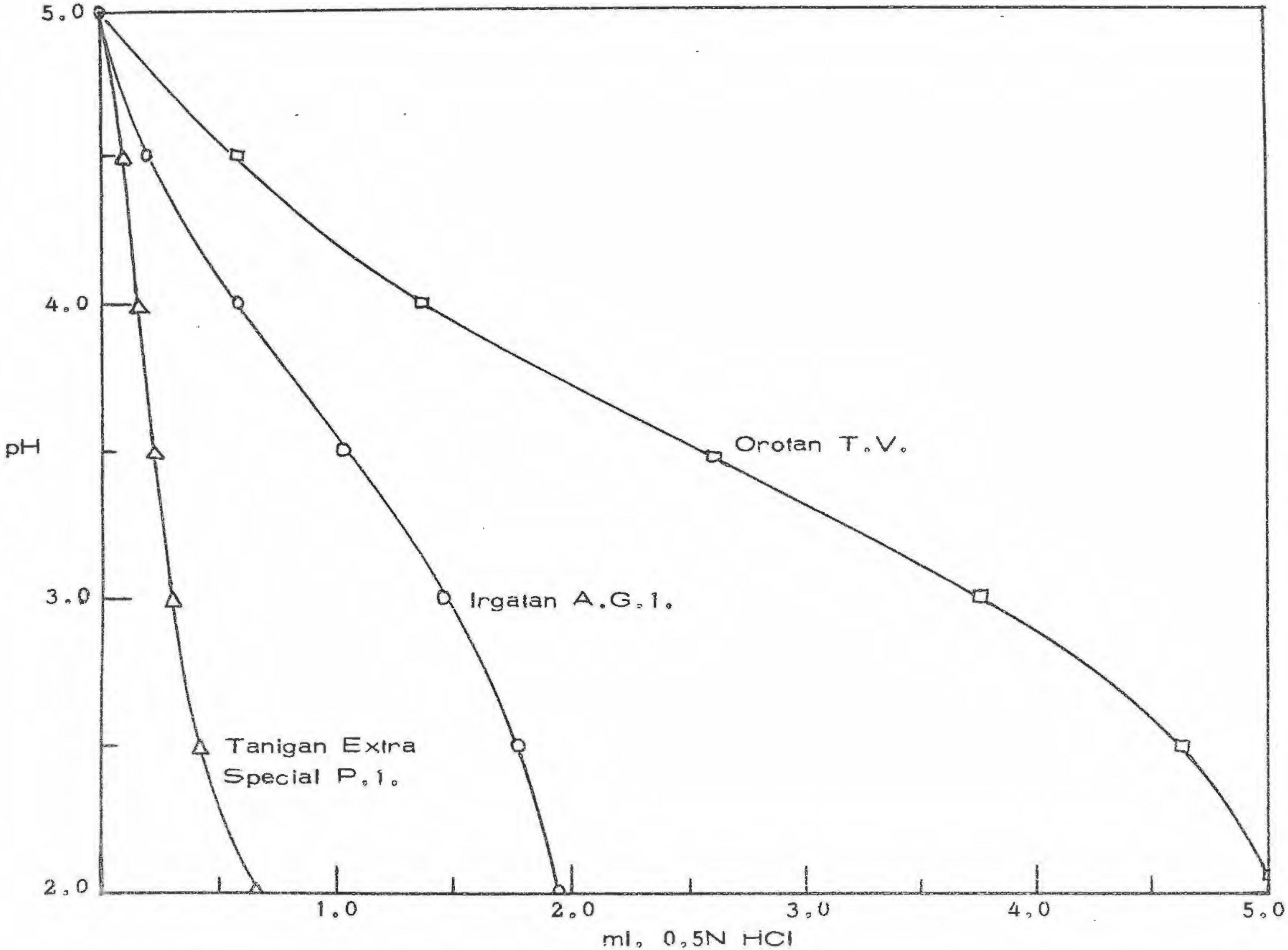


Figure 1. Titration curves of 50 ml. aliquots of syntan solution each made up to contain 25% tannins and initially adjusted to pH 5.0 with NaOH.

Table X
Dyeing Characteristics
(high scores indicate level dyeing)

| pH of blend | Composition of retanning blend | | | | Mean |
|---|---|---|---|---|---|
| | Wattle only | Irgatan AG1 Wattle | Orotan TV Wattle | Tanigan Ex.Sp.P1 Wattle | |
| pH 3.5 | 2.25 | 1.19 | 1.81 | 2.12 | 1.84 |
| pH 5.0 | 2.50 | 2.25 | 1.81 | 2.69 | 2.31 |
| Mean | 2.37 | 1.72 | 1.81 | 2.40 | 2.07 |

The dyeing characteristics of leather retanned with Orotan TV + wattle blends were unaffected by pH of retannage but in all other cases high pH yielded more evenly dyed leather.

## CONCLUSIONS

Variations in the retannage were much larger than any brought about during neutralising, and no statistically significant effects of the latter process were found except in the case of dyeing characteristics, where Orotan N yielded a very uniformly dyed leather.

It has been found that a normal temperature, 20°C, is superior to a high temperature, 40°C, for producing optimum grain strength, although this may in part be a reflection of the greater plumping of the leather retanned at high temperature.

The three syntans studied were not used under the conditions recommended by their manufacturers, but were compared under certain specific conditions. Although all three syntans are recommended by their manufacturers as being suitable for combining with wattle they have widely differing properties as far as buffering capacity is concerned. "Orotan TV" in particular is very highly buffered and from inspection of the titration curve, Fig. 1, almost certainly contains a large amount of formate ion.

The shrinkage temperatures were in all cases very high and are all satisfactory.

were presented in Research Bulletin No. 212, (see page 98).

## RESULTS

### A. CHANGES IN PHYSICAL PROPERTIES ON ACCELERATED AGEING

The main properties that are likely to change on ageing are buckle tear strength, load and extension at grain crack, and shrinkage temperature. By determining changes in the physical properties, those factors which markedly alter the rate of deterioration on ageing are shown up. The conditions for accelerated ageing were storage at 47°C and 95+ % r.h. for 3 weeks, after which the leathers were dried out, conditioned and tested.

#### Difference in Buckle Tear Strength between Artificially Aged and Unaged Leathers

Differences in the rate of deterioration are mainly associated with the composition of the retanning blend. Thus, for the smaller amount of deterioration under the conditions of this test the syntans should be added prior to the wattle, but, where only wattle is used as the retanning agent, the split feed is deleterious, less deterioration occuring where the wattle was added in one lot. This effect is shown in Table I.

Table I

Fall in Buckle Tear Strength, Accelerated Ageing (lb./in.)

| Retanning material added | Composition of Retanning Blend | | | | Mean |
|---|---|---|---|---|---|
| | Wattle | Irgatan + Wattle | Orotan + Wattle | Tanigan + Wattle | |
| all together | 192 | 217 | 200 | 217 | 206 |
| 25% then 75% | 217 | 191 | 181 | 179 | 192 |
| Mean | 204 | 203 | 190 | 198 | 199 |

The effect of the syntans on the rate of deterioration are dependent on the pH of application of the retanning blend. This interaction is shown in Table II. In general, at the higher pH the rate of deterioration is reduced, but in the case of Orotan TV the effect of the syntan is superior at the pH where buffering is greatest, i.e. pH 3.5.

Table II
Fall in Buckle Tear Strength, Accelerated Ageing (lb./in.)

| pH of Blend | Composition of Retanning Blend | | | | Mean |
|---|---|---|---|---|---|
| | Wattle | Irgatan + Wattle | Orotan + Wattle | Tanigan + Wattle | |
| pH 3.5 | 200 | 242 | 181 | 208 | 208 |
| pH 5.0 | 209 | 165 | 201 | 188 | 191 |
| Mean | 204 | 203 | 191 | 198 | 199 |

The temperature of the retanning liquor also greatly influenced the durability of the leather. The higher temperature of the retanning liquor resulted in a much larger drop in the buckle tear strength compared with the lower temperature. It is interesting to note that the higher temperature also resulted in a lower pH value for the spent retan liquors (see Research Bulletin No. 212).

Difference in Load at Grain Crack between Artificially Aged and Unaged Leathers

Less deterioration occurred in the samples that had been retanned with a syntan in the blend. Whilst the temperature of retanning had little influence on the deterioration of these samples, the effect on those retanned with only wattle was considerable. This interaction is shown in Table III.

Table III
Fall in Load at Grain Crack, Accelerated Ageing (lb./in.)

| Temperature of Retan Liquor | Composition of Retanning Blend | | | | Mean |
|---|---|---|---|---|---|
| | Wattle | Irgatan + Wattle | Orotan + Wattle | Tanigan + Wattle | |
| 20°C | 600 | 438 | 320 | 444 | 450 |
| 40°C | 463 | 388 | 331 | 462 | 411 |
| Mean | 531 | 413 | 325 | 453 | 430 |

The addition of the syntan prior to the wattle did not increase the durability of the leather as determined by this test except in the case of the Orotan TV. In this case a considerable improvement was effected by the addition of the syntan before the wattle. The effects of the retan additions are given in Table IV.

Table IV

Fall in Load at Grain Crack, Accelerated Ageing (lb./in.)

| Retanning material added | Composition of Retanning Blend | | | | Mean |
|---|---|---|---|---|---|
| | Wattle | Irgatan + Wattle | Orotan + Wattle | Tanigan + Wattle | |
| all together | 519 | 388 | 375 | 412 | 423 |
| 25% then 75% | 544 | 438 | 275 | 494 | 438 |
| Mean | 531 | 413 | 325 | 453 | 430 |

The efficacy of the syntans in resisting deterioration depended to some extent on the pH of application of the retanning blend. In the case of Irgatan AG1 the higher pH resulted in less deterioration and with Orotan TV the lower pH gave optimum durability. With Tanigan Extra Special P1 the results were unaffected by pH. The wattle tanned leathers deteriorated more when tanned at the lower pH. The average figures for each of these tannages is given in Table V.

Table V

Fall in Load at Grain Crack, Accelerated Ageing (lb./in.)

| pH of Blend | Composition of Retanning Blend | | | | Mean |
|---|---|---|---|---|---|
| | Wattle | Irgatan + Wattle | Orotan + Wattle | Tanigan + Wattle | |
| pH 3.5 | 575 | 431 | 306 | 450 | 440 |
| pH 5.0 | 487 | 394 | 344 | 456 | 420 |
| Mean | 531 | 413 | 325 | 453 | 430 |

None of the neutralising factors had a significant effect on the deterioration of the leathers.

Difference in Extension at Grain Crack between Artificially Aged and Unaged Leathers

The neutralising agents made a small but significant difference in this case. The use of sodium or ammonium bicarbonate resulted in a greater reduction in extension than when calcium formate or Orotan N were used. The average fall in extension at grain crack for the four neutralising agents are: sodium bicarbonate, 0.87 mm.; ammonium bicarbonate, 0.87 mm.; calcium formate 0.75 mm.; and Orotan N, 0.74 mm.

The composition of the retanning blend had a very important effect on the decrease of extensibility on ageing. The use of syntans in the blend greatly reduced deterioration. Orotan TV was especially effective, particularly if it was added prior to the wattle retanning material. The average effect of each of the tannages is given in Table VI.

Table VI
Fall in Extension at Grain Crack, Accelerated Ageing, mm.

| Retanning material added | Composition of Retanning Blend | | | | Mean |
|---|---|---|---|---|---|
| | Wattle | Irgatan + Wattle | Orotan + Wattle | Tanigan + Wattle | |
| all together | 1.12 | 0.74 | 0.62 | 0.77 | 0.81 |
| 25% then 75% | 1.18 | 0.86 | 0.31 | 0.85 | 0.80 |
| Mean | 1.15 | 0.80 | 0.46 | 0.81 | 0.80 |

Difference in Ts of Artificially Aged and Unaged Leathers

Soon after manufacture all the leathers had satisfactory, high shrinkage temperatures, the average value being 123°C. Accelerated ageing resulted in a fall in the Ts of about 18°C, but some of the retanning factors affected the extent to which the Ts has fallen. All the syntans and especially Orotan TV reduced the fall in Ts when added before the wattle, but little benefit was derived when added in admixture with the wattle. The effect of the syntans compared with wattle is given in Table VII.

Table VII

Fall in Shrinkage Temperature, Accelerated Ageing, °C.

| Retanning material added | Composition of Retanning Blend | | | | Mean |
|---|---|---|---|---|---|
| | Wattle | Irgatan + Wattle | Orotan + Wattle | Tanigan + Wattle | |
| all together | 18.4 | 19.7 | 17.6 | 19.2 | 18.7 |
| 25% then 75% | 20.7 | 18.3 | 14.5 | 18.5 | 18.0 |
| Mean | 19.5 | 19.0 | 16.0 | 18.8 | 18.3 |

The temperature of retanning and the pH of the retanning blend both affect the extent of the fall in Ts, the high temperature resulting in a greater loss in Ts (40°C tannage, $\Delta$Ts=19.4°C; 20°tannage, $\Delta$Ts=17.3°C), and the low pH of tannage has resulted in a larger fall in Ts (pH 3.5 tannage, $\Delta$Ts=19.1°C; pH 5.0 tannage, $\Delta$Ts= 17.6°C).

## B. CHANGES IN PHYSICAL PROPERTIES ON NATURAL AGEING

Natural ageing was effected by storing the leather samples at 65% r.h. and 20°C for 8 months. The samples were tested for buckle tear load, and load and extension at grain crack. The results are given as differences from the original values.

### Difference in Buckle Tear Strength between Naturally Aged and Unaged Leathers

Differences in the buckle tear strength between unaged and naturally aged leathers were associated with only the composition of the retanning blend. In each case the application of the syntan prior to the wattle resulted in less deterioration than when the blend was added in one lot. This effect is given in Table VIII.

Table VIII

Fall in Buckle Tear Strength, Natural Ageing, (lb./in.)

| Retanning material added | Composition of Retanning Blend | | | | Mean |
|---|---|---|---|---|---|
| | Wattle | Irgatan + Wattle | Orotan + Wattle | Tanigan + Wattle | |
| all together | 159 | 140 | 169 | 188 | 164 |
| 25% then 75% | 166 | 106 | 113 | 100 | 121 |
| Mean | 162 | 123 | 141 | 144 | 142 |

Difference in Load at Grain Crack between Naturally Aged and Unaged Leathers

All the retanning factors influenced the deterioration on natural ageing as determined by the load at grain crack. Less deterioration occurred in the samples that had been retanned with a syntan in the blend. Greater deterioration occurred in these samples when they were retanned at the high temperature. Those that were retanned with only wattle at the high temperature deteriorated to a lesser extent. This interaction is given in Table IX.

Table IX
Fall in Load at Grain Crack, Natural Ageing (lb./in.)

| Temperature of retan liquor | Composition of Retanning Blend | | | | Mean |
|---|---|---|---|---|---|
| | Wattle | Irgatan + Wattle | Orotan + Wattle | Tanigan + Wattle | |
| 20°C | 337 | 212 | 119 | 262 | 230 |
| 40°C | 269 | 256 | 237 | 331 | 276 |
| Mean | 303 | 234 | 178 | 297 | 253 |

The addition of the syntan before the wattle did not improve the durability of the leathers, except in the case of the Orotan TV. In this case the deterioration was considerably reduced. The mixture of the syntans with the wattle gave a slight improvement in the resistance to deterioration. These effects are given in Table X.

Table X
Fall in Load at Grain Crack, Natural Ageing (lb./in.)

| Retanning material added | Composition of Retanning Blend | | | | Mean |
|---|---|---|---|---|---|
| | Wattle | Irgatan + Wattle | Orotan + Wattle | Tanigan + Wattle | |
| all together | 287 | 212 | 206 | 244 | 237 |
| 25% then 75% | 319 | 256 | 150 | 350 | 269 |
| Mean | 303 | 234 | 178 | 297 | 253 |

The higher pH of retanning had resulted in less deterioration with all retanning materials, but the effect on the 100% wattle tannage was small compared with the effect on the leathers tanned with syntans in the blend. This interaction is given in Table XI.

Table XI

Fall in Load at Grain Crack, Natural Ageing (lb./in.)

| pH of Blend | Composition of Retanning Blend | | | | Mean |
|---|---|---|---|---|---|
| | Wattle | Irgatan + Wattle | Orotan + Wattle | Tanigan + Wattle | |
| pH 3.5 | 312 | 262 | 225 | 344 | 286 |
| pH 5.0 | 294 | 206 | 131 | 250 | 220 |
| Mean | 303 | 234 | 178 | 297 | 253 |

Difference in Extension at Grain Crack between Naturally Aged and Unaged Leathers

Under the mild conditions of storage some of the leathers actually had an increased extension at grain crack compared with the leathers tested soon after manufacture. Over-all there had been a fall in the extension at grain crack, but the type of neutralising agent affected the degree of deterioration. On average the leather neutralised with calcium formate plus sodium bicarbonate deteriorated less than the others. The loss in extension for the four neutralising materials is: sodium bicarbonate, 0.24 mm.; ammonium bicarbonate, 0.30 mm.; calcium formate + sodium bicarbonate, 0.02mm.; and Orotan N, 0.31 mm.

The composition of the retanning blend was also most important, but the effect of each on the resistance to deterioration was dependent on the manner in which the retanning materials were added. Wattle tanned leather has shown the greatest deterioration, whereas leather retanned with blends containing Irgatan AG1 and Orotan TV were actually slightly more extensible than the original leathers. This effect is shown in Table XII.

Table XII

Fall in Extension at Grain Crack, Natural Ageing, mm.

| Retanning material added | Composition of Retanning Blend | | | | Mean |
|---|---|---|---|---|---|
| | Wattle | Irgatan + Wattle | Orotan + Wattle | Tanigan + Wattle | |
| all together | 0.48 | -0.48 | 0.33 | 0.05 | 0.09 |
| 25% then 75% | 1.56 | 0.10 | -0.73 | 0.40 | 0.33 |
| Mean | 1.02 | -0.19 | -0.20 | 0.22 | 0.21 |

## DISCUSSION

Of the factors varied, by far the largest effects have resulted from changes in the composition of the retanning material. In nearly every case enhanced durability has resulted from the inclusion of syntans in the retanning blend, Orotan TV being particularly effective both under warm humid conditions and on natural ageing. The effect of the syntans, however, depended on other conditions during retanning. In general the high temperature of retanning has resulted in less durable leather, and this is usually the case with tannages carried out at low pH values.

The addition of the syntan to the chromed pelt before adding the wattle in tannages combining the two tanning materials, invariably resulted in leather with greater durability than leathers retanned with blends added in one lot. In the case of the 100% wattle retannages superior results were obtained if all the wattle was added at once.

The variations in the neutralising procedure has not much affected the durability of the leather. There is evidence, however, that the use of a complexing agent or of Orotan N (a neutralised sulphonic acid syntan) in the neutralising gave added durability. The latter may possibly be improved if some alkali is also used, since the pH of the exhaust neutralising solution was rather low in this case. The temperature of neutralising had little effect, but the indications are that neutralising at elevated temperature was harmful.

The relationship between natural and accelerated ageing seems to be fairly close particularly with regard to strength characteristics of the leathers.

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# R.B. 261. CHROME RETAN LEATHER : THE EFFECT OF COMPLEXING AGENTS AND SYNTANS ON THE STABILITY OF CHROME RETAN LEATHER

by

D.A. Williams-Wynn.

## SUMMARY

An investigation has been made of the effect of various additives in the neutralising, of a pre-retan fatliquor, and of blending a syntan with wattle extract, on the properties and ageing characteristics of chrome-retan leather. The most important factor was the replacement of 25% of the wattle tans with Orotan TV. This resulted in strong, flexible leather with excellent ageing characteristics. The introduction of complexing agents during neutralising largely invalidated the accelerated ageing test for predicting the durability of chrome-retan leather, but their presence to a greater or lesser extent improved the physical characteristics of the leather, and improved the durability on natural ageing. Combination of both complexing agents in the neutralising and syntan in the retanning was not a success. The pre-retan fatliquor gave leather of greatly enhanced initial strength and was of use for maintaining extensibility of grain, but was not effective in maintaining strength on ageing.

## INTRODUCTION

Previous reports [1,2,3] have shown that the use in neutralising of materials which complex strongly with chromium, produces leather with enhanced physical properties and in some cases greater durability on storage. However, as a result of early work [4], durability on storage was determined by the accelerated ageing test, which, although accurate for leathers containing no organic anions, does not give a true reflection of the deterioration to be expected from leathers containing complexing agents and/or syntans [5,6]. In some of the early work materials were condemned which were found to give little or no improvement in the durability of chrome-retan leather and in some cases accelerated the deterioration under the warm, humid conditions of the accelerated ageing test. It was thought desirable, therefore, to re-investigate the use of these materials under ageing conditions of normal temperature and humidity.

Syntans have been used with some success in blends with wattle for retanning [7,8], and have also had some slight effect when used for neutralising [3,7], nevertheless, the effect on durability of syntans in conjunction with complexing agents has not been studied in detail, although the use of formate masking has been of advantage [7]. In the present work, a syntan, Orotan TV, which was found to be satisfactory, has been used in conjunction with complexing agents in the neutralising to determine the effect on ageing. Leathers were stored at both high temperature and high humidity, and normal temperature and humidity.

Pre-retan fatliquoring has been found to be beneficial in increasing the durability [9,10], and in this experiment use was made of an acid- and chrome-resistant fatliquor before the retannage to discover whether there were any benefits to be derived from such a fatliquor. It had been discovered [10], however, that fatliquors based on this type of oil are not suitable for the purpose.

Process Variables

A Neutralisation

$A_1$ 1% Borax
$A_2$ 1% Ca formate + 1% borax
$A_3$ 1% Calgon + 1% borax
$A_4$ 1% Sulphophthalate + 1% borax.

B Pre-retan Fatliquor

$B_1$ None
$B_2$ 1% Grassan ET (acid- and chrome-resistant)

C Retannage

$C_1$ 10% Wattle Extract
$C_2$ 5% Orotan TV, 7½% Wattle Extract

Preparation of the Samples

A side in the blue shaved to 1½ mm. was obtained from a member firm. 32 Samples 6 in. × 6 in. were cut and numbered, and randomised. The samples were sorted into four groups of eight samples, and were neutralised with four different neutralising materials as given in factor A. Each group was washed in running water for 15 min. then neutralised in 100% of water for 30 min., and finally washed in running water for 30 min.

Half of each of the neutralised samples were combined and given a pre-retan fatliquor with 1% Grassan ET in 100% water at 50°C for 30 min. The remaining pieces were washed in warm water (50°C) for 30 min.

All the samples were divided into two groups for retanning with the materials given in factor C, each group having samples representative of all the treatments in factors A and B. Retannage was effected by drumming the well-washed pieces with either 10% wattle extract in 100% float for 45 min., or 5% Orotan TV in 50% float for 15 min. then 7½% wattle extract in 50% float added and drumming continued for 30 min.

The retanned samples were combined, well washed in cold water, then in warm water at 45-50°C. The float was reduced to 100% and an emulsion of 1½% sulphated whale and 2% raw whale oil added and drummed until clear. After fatliquoring the pieces were piled over-night then slicked out and nailed to dry. When dry each was damped back, staked lightly by hand and redried.

The leathers were assessed for flexibility and specimens cut for buckle tear and lastometer measurements initially, and after 9 months natural and 3 weeks accelerated ageing. The analysis of variance technique was used to determine the significance of the results.

## RESULTS

### Flexibility

The samples were assessed manually for flexibility and divided into 7 groups. Scores were alotted on the basis 0 for firm leathers to 6 for the softest, most flexible leathers. The most interesting result was the observation that the additional oil offered in the pre-retan fatliquor had no influence on the flexibility of the leather.

The materials used in neutralising had a slight influence on the flexibility, softness decreasing in the order: borax 31; calcium formate and borax, 26; calgon and borax, 25; and sulphophthalate and borax, 20.

The type of retanning material had a very significant effect on the flexibility, the blend of Orotan TV and wattle giving much softer leather than the all wattle retannage. However the effect of the retanning material is dependent on the type of neutralising material used. This interaction is given in Table I.

Table I

The Effect of the Composition of Neutralising and Retanning Materials on the Flexibility (high numbers flexible)

| Retanning material | Composition of Neutralising Materials | | | | Total |
|---|---|---|---|---|---|
| | Borax | Ca formate + Borax | Calgon + Borax | Sulphophthalate + Borax | |
| Wattle | 15 | 5 | 8 | 10 | 38 |
| Orotan TV+Wattle | 16 | 21 | 17 | 10 | 64 |
| Total | 31 | 26 | 25 | 20 | 102 |

From the table it will be seen that the addition of formate or Calgon to the neutralising increases the firmness of wattle retanned leather, but the presence of formate increases the flexibility of leather retanned with Orotan TV/Wattle blend. This is interesting since it has been shown[7,11] that Orotan TV buffers strongly at pH 3.7, which indicates the presence of formate in the syntan. Hence, additional formate from the neutralisation seems to reinforce the effect of the formate in the syntan, increasing its effectiveness.

Buckle Tear Load

The pre-retan fatliquor considerably increased the buckle tear load, the average values being no pre-retan fatliquor, 535 lb./in; 1% Grassan ET before retanning 745 lb./in. There is evidence that formate in the neutralising together with the pre-retan fatliquor considerably increased the buckle tear load, but formate without the Grassan ET had no effect. This interaction is given in Table II.

Table II

The Effect of the Composition of the Neutralising Materials and Pre-retan Fatliquor on Buckle Tear Load (lb./in.)

| Pre-retan fatliquor | Composition of Neutralising Materials | | | | Mean |
|---|---|---|---|---|---|
| | Borax | Ca formate + Borax | Calgon + Borax | Sulphopththalate + Borax | |
| None | 500 | 500 | 550 | 600 | 535 |
| 1% Grassan ET | 750 | 875 | 650 | 700 | 745 |
| Mean | 625 | 690 | 600 | 650 | 640 |

Lastometer Load at Grain Crack

Neither the pre-retan fatliquor nor the composition of the retanning material had any significant effect on the load at grain crack. The type of neutralising material, however, did have a significant effect on the load; Calgon increased the strength by about 10%. The average values for the four neutralising treatments were: sodium bicarbonate, 1380 lb./in.; calcium formate and sodium bicarbonate, 1310 lb./in.; Calgon and sodium bicarbonate, 1510 lb./in.; and sulphophthalate and sodium bicarbonate 1420 lb./in.

Lastometer Extension at Grain Crack

Of the factors varied, only the composition of the neutralising agents and of the retanning materials affected the extension at grain crack. The pre-retan fatliquor had no influence on this property.

The greatest extension was obtained when only sodium bicarbonate was used for neutralising, the least extensible leather was obtained from the neutralising mixture containing formate. Average values for the four neutralising procedures are: sodium bicarbonate, 9.1 mm.; calcium formate and sodium bicarbonate, 8.5 mm.; Calgon and sodium bicarbonate, 8.8 mm.; and sulphophthalate and sodium bicarbonate, 8.7 mm.

Replacement of 25% of the wattle by syntan in the retanning gave more extensible leather, average values being all wattle retannage, 8.6 mm.; Orotan TV/wattle blend, 8.9 mm.

Ageing Characteristics

A. Natural Ageing

Leather loses strength and extensibility on ageing, and to determine which factors have influenced the degree of deterioration, calculations are based on the difference between the strengths before and after ageing.

Buckle Tear Load

The strength of the leathers was reduced by an average of 16% on 9 months natural ageing. All the treatments in the neutralising affected the rate of deterioration. The only process which significantly reduced the deterioration of leathers retanned with wattle only was that containing sulphophthalate. When the leathers had been retanned with the blend of

Orotan TV and wattle, deterioration was considerably reduced compared with the wattle tannage, but the presence of the complexing agents impaired some of this improvement. This interaction is given in Table III.

Table III

The Influence of the Composition of Neutralising Materials and Retanning Agent on Deterioration after Natural Ageing (Buckle Tear as % of Original)

| Retanning material | Composition of Neutralising Materials | | | | Mean |
|---|---|---|---|---|---|
| | Borax | Ca formate + Borax | Calgon + Borax | Sulphophthalate + Borax | |
| Wattle | 78 | 80 | 80 | 83 | 80 |
| Orotan TV+Wattle | 94 | 82 | 81 | 88 | 87 |
| Mean | 87 | 81 | 80 | 86 | 84 |

The pre-retan fatliquor did not influence the degree of deterioration.

Lastometer Load at Grain Crack

The average percentage deterioration as determined by this test was very small, and none of the factors investigated in this work significantly influenced the amount of deterioration. In the type of neutralising material a tendency to greater resistance to deterioration was observed in the case of the sulphophthalate.

Lastometer Extension at Grain Crack

As with the previous section, none of the factors significantly influenced the effect of ageing on the extension at grain crack. The average loss of extension was 12.5% (1.2 mm.). In this case a trend in favour of both Calgon and sulphophthalate was discernable.

B. Accelerated Ageing

Specimens were cut from each sample, and aged at 48°C and 95+ % r.h. for 3 weeks when they were dried and reconditioned for test. The effect of each factor on the deterioration of the leather is measured as the difference of each property from the original.

Buckle Tear Load

A most significant feature is the effect of the pre-retan fatliquor. The addition of Grassan ET caused a greater rate of deterioration under the conditions of the accelerated ageing test than was observed in those leathers which had not received the pre-retan fatliquor. The average values as a percentage of the original strength for the two levels of the factor are: no pre-retan fatliquor, 72.2%; fatliquored with Grassan ET, 69.7%.

Another very significant factor is the composition of the retanning mixture. The blend of Orotan TV and wattle produced leather which deteriorated to a much smaller extent than that retanned with wattle only. The average percentage of the original strength for each are: wattle only, 66.6%, Orotan TV and wattle, 74.3%.

The complexing agents used in the neutralising did not cause a significant difference in the rate of deterioration, but it was observed that the presence of formate did cause a slightly increased rate of deterioration.

Lastometer Load at Grain Crack

Loss of grain strength of the leathers which had had the pre-retan fatliquor was reduced compared with the other leathers. Percentage values of the original strength were 83.3 and 79.2% respectively. The inclusion of Orotan TV in the retanning blend caused less deterioration than was found in leathers retanned wholly with wattle. Average values as percentage of the original are 84.6 and 79.4% respectively. The neutralising materials also affected the rate of deterioration but the extent to which deterioration occurred was dependent on the type of retanning material. The interaction is given in Table IV.

Table IV

The Effect of Composition of the Neutralising Materials and Retanning Mixture on Deterioration after Accelerated Ageing (Lastometer Load % of Original)

| Retanning material | Composition of Neutralising Materials | | | | Mean |
|---|---|---|---|---|---|
| | Borax | Ca formate + Borax | Calgon + Borax | Sulphophthalate + Borax | |
| Wattle | 82.6 | 78.5 | 81.4 | 75.3 | 79.3 |
| Orotan TV+Wattle | 87.3 | 85.7 | 82.7 | 82.4 | 84.6 |
| Mean | 84.9 | 82.1 | 82.1 | 78.9 | 82.0 |

Lastometer Extension at Grain Crack

The loss of extensibility after accelerated ageing was reduced when Orotan TV was used in a blend with wattle for retanning. The average values as percentage of the original extension for the two retanning mixtures are: wattle, 84.7; Orotan TV and wattle, 87.2%. The pre-retan fatliquor also reduced the loss in extensibility, average values being: none, 85.1%; 1% Grassan ET, 86.8%. None of the variables in the neutralising caused a significant difference in the loss of extensibility.

## DISCUSSION AND CONCLUSIONS

The results of the present work have largely confirmed previous work on the deterioration of chrome-retan leather. The use of a suitable syntan in a blend with or preferably added prior to the vegetable tanning material has again been shown to be a most important factor in producing strong, flexible chrome-retan leather which has excellent ageing characteristics. The syntan not only produced stronger leather but also reduced the rate at which deterioration occurred. Various levels of the other factors caused an increase in the original strength and extensibility, but deterioration occurred at a greater rate, so that the aged values were reduced to the equivalent of the control and in some cases even below. One notable exception was the effect of the pre-retan fatliquor in maintaining the extensibility even after the rigorous conditions of the accelerated ageing test.

The use of sulphophthalate in neutralising, whilst being most effective in maintaining strength on natural ageing was rather disappointing when the leathers were aged at high temperature and high humidity. Calgon did not cause excessive deterioration under the conditions of the accelerated ageing test, but was found to be not very effective in reducing deterioration on natural ageing. Formate was as effective as Calgon in reducing deterioration on natural ageing, but considerable strength was lost during the accelerated ageing test.

The addition of certain complexing agents during neutralising can be recommended if subsequent retannages are to be based wholly on wattle. When suitable syntans are used in conjunction with the wattle extract for retanning no advantage is to be gained by including complexing agents in the neutralising. A pre-retan fatliquor has been found to be of doubtful value except in maintaining extensibility which, from a shoe-making point of view is most important, and for improving the buckle tear strength. Since it is not known whether the best type of emulsion was used for the pre-retan fatliquor, it is possible that substantially improved results might have been obtained if different fatliquors had been used.

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# R.B. 181. INFLUENCE OF THE DEGREE OF RETANNAGE ON THE PROPERTIES OF CHROME-RETAN LEATHER

by

R.L. Sykes and D.A. Williams-Wynn.

## SUMMARY

The work presented in this report is based on recommendations made to the Leather Institute by the Tanners' Research Committee. The main item studied has been the effect of increasing, by small increments, the amount of wattle extract used for retanning chrome leather. It was found that the strength showed a progressive decline with increasing amounts of retannage, but that this reached negligible proportions after 10-12% wattle tannin had been used. The nature of the chromed stock used was also varied. Previous findings that a 33% basic chrome-retannage was preferable has been confirmed. Some increase in strength was noted when smaller amounts of chrome were offered, and this was also found to result in more efficient uptake of $Cr_2O_3$. Formate masking indicated only a slight trend towards increasing strength in the retanned leather. The conditions of retannage were important, particularly the duration of retannage which should be kept as short as possible. There was some indication that for a given type of pelt there was a close relationship between buckle tear strength and the pH of 5% aqueous extract. Ageing appeared to alter both properties proportionately.

## INTRODUCTION

Previous work on this project has been recorded in Research Bulletins Nos. 175 and 178 and the present report is on two further experiments which have since been carried out to obtain more information on the manufacture of this type of leather with particular reference to its physical strength and ageing characteristics.

### Preliminary Experiment on Liming Conditions

Production conditions in tanneries frequently necessitate that rapid drum liming techniques are employed in the manufacture of upper leather. Unfortunately, these require the presence of quite high sulphide concentrations which are not conducive to good grain when low quality hides are used. Various reports from North America have indicated that paddle liming techniques are frequently used for manufacturing retan leather. Quite recently Shuttleworth[1] has developed a two-stage liming process where the hair is removed by drum pasting under virtually neutral conditions and the opening up of the hide is subsequently carried out in pits with white lime. The process had in view the selection of hides after unhairing but prior to liming and has been shown in works trials to give satisfactory results for both sole and chrome side leather. Its application to retan leather has been studied in the present experiment. Finally a development of this process has been included for comparison. In this the hides were given a quick wash in water to remove surplus salt and then soaked in calcium chloride for 24 hours, since this material is well known for its ability not only to disperse inter-fibrillary material but also to act as a swelling assistant. Unhairing was effected by the addition of sodium sulphide to the soaked hides under conditions similar to those suggested by Shuttleworth. Unhairing was virtually complete after 1 h. No conventional liming was subsequently carried out.

For this experiment medium weight cattle-hide was used and cut into blocks prior to soaking; these were randomised between the four liming techniques which are detailed below, together with the soaking conditions.

| Process | Soaking | Liming |
|---|---|---|
| I (Paddle liming) | 24 h. in water, occasional movement | 6% lime, 3/4% sodium sulphide in 400% float for 4 days. Occasional movement in paddle, say 5 min. 3 times/day. |
| II (Drum liming) | as I | 4% lime, $2\frac{1}{2}$% sodium sulphide lumps in 200% float for 24 h. periodic movement of drum, say 5 min./h. |
| III (Rapid unhairing) | as I | Paste unhairing 2% calcium chloride, 2% sodium sulphide in 20% water. Run for $\frac{1}{2}$ h. hair removed and hides placed in fresh white lime for 24 h., floated twice. |

| Process | Soaking | Liming |
|---|---|---|
| IV (Ultra rapid) | $\frac{1}{2}$ h. wash in water, 24 h. in 5% calcium chloride solution 300% float | 2% calcium chloride, 3% sodium sulphide in 20% water added to drained soaked hides. Drummed 1 h. |

Subsequent to liming the hides were delimed, pickled, tanned with a 33% basic chrome liquor, split and retanned with 10% wattle extract from a 200° Bk. solution. After fatliquoring the leathers were paste dried, conditioned and staked.

There were 32 individual pieces of leather which had been limed by each of the 4 methods, 128 pieces in all. They were evaluated by the lastometer, and the average grain strengths are recorded in Table I.

Table I

Load at Grain Crack of Differently Limed Leather

| Liming method | | |
|---|---|---|
| I | Paddle liming | 792 lb./in. |
| II | Conventional drum liming | 608 lb./in. |
| III | Rapid unhairing followed by flat liming | 716 lb./in. |
| IV | Calcium chloride soak, rapid unhairing no liming | 599 lb./in. |

The results shown above indicate the superiority of paddle liming for producing a retan leather of high grain strength. Whilst the process evolved by Shuttleworth which separates unhairing from liming appears to be better than the conventional drum liming, more detailed work on this method may well produce methods of improving it further. The process which eliminated lime completely cannot be considered as an improvement at the present time.

## MAIN EXPERIMENT

Having found from the previous experiment that the two-stage liming technique gave reasonably high strength leather, a further experiment was planned on a factorial basis to study some of the other factors which are liable to influence the strength of retan leather.

Factors Studied in the Experiment

Analyses at L.I.R.I. of many American retan leathers had indicated that their chromic oxide contents were frequently very low, thus it seemed advisable to study the effect of lowering the chrome content of retan leather. Furthermore, masking is frequently practiced overseas and this may be of assistance in making a more stable chrome leather less liable to deteriorate. A previous experiment [2] had indicated that a retan leather chromed with a 33% basic chrome salt was stronger than one chromed with a 50% basic liquor; for further confirmation of this point the two liquors were again compared in the present experiment. The members of the Tanners' Research Committee suggested that the effect of increasing the degree of retannage by a number of small increments be studied to determine whether there were any marked breaks in the strength/degree of retannage curve. Finally two variations in the method of applying the wattle extract were studied: these were, from a long as against a short float, and with long and short drumming times. Details of the factors varied and the statistical plan are given below.

A Masking of Chrome Liquor

(1) none
a 1 mole sodium formate/mole $Cr_2O_3$

B Basicity of Chrome Liquor

(1) 33% basic
b 50% basic

C Amount of Chrome Offered

(1) 1.25% $Cr_2O_3$ on limed wt.
c 2% $Cr_2O_3$ on limed wt.

DEF Amount of Tan Offered

(1) 2% actual tan on blue wt.
d 4%
e 6%
de 8%
f 10%
df 12%
ef 14%
def 16%

G Concentration of Extract Offered

(1) from 50% float
g from 200% float

H Drumming Time for Retannage

(1) 1 h.
h 6 h.

Statistical Plan

A half replicate of a $2^8$ factorial = 128 samples with defining contrast ABCDEFGH. The samples were cut in 4 blocks of 32 samples each, and interactions confounded with blocks were:

ABEF = CDGH
ACEG = BDFH
BCFG = ADEH

Experimental Tannages

A wet salt hide was soaked for 24 h. and then unhaired by drumming with a paste of 2% calcium chloride and 2% sodium sulphide in a 20% float for 40 min. The hair was removed by working over the beam and the unhaired hide was flat limed for 2 days. The hide was split after 1 day in lime. The limed hide was cut into the small pieces, each of which was numbered, and then sorted for the eight different tannages. The tanned leathers were neutralised with 1 1/4% sodium bicarbonate and then sorted into 16 lots for retanning. From each lot half of the samples were removed after I hour, and half the liquor was run off so that the correct liquor-to-goods ratios were maintained. Drumming was continued for a further 5 hours.

Immediately after completion of a retannage the leathers were washed for 5 min. in running water, dyed with 2% naphthalene leather green for 10 min., using 1% formic acid to help exhaust the dye for a further 5 min. (Note this dyeing technique was employed to obtain deep surface colouring, thus rendering lastometer testing more accurate). Fatliquoring was in two stages, the first was an anionic emulsion consisting of:-

2% Sulphated whale oil
½% Whale oil
1½% Mineral oil
0.2% Sulphated fatty alcohol

This was topped in a fresh liquor consisting of ½% Lipamin liquor O (B.A.S.F.). The leathers were all paste dried, damped back in sawdust and hand-staked.

# RESULTS

## Chemical Analyses

The leathers were analysed for their content of chromium oxide. They were sorted for the following factors and chrome contents determined in order to assess the effect of the factors on the chrome content of the leather: amount of chrome offered, basicity, masking, concentration of retan extract, length of retanning time.

As might be expected, the amount of chrome offered had a very significant effect, the average results were:-

1.25% $Cr_2O_3$ offered on limed wt. - 3.09% $Cr_2O_3$ in leather
2.0% $Cr_2O_3$ offered on limed wt. - 3.78% $Cr_2O_3$ in leather.

The basicity of the tannage made no difference to the uptake of chromium, the mean figures being 3.43% $Cr_2O_3$ for the 33% basic tannage and 3.44% $Cr_2O_3$ for the 50% basic tannage. Masking had no significant effect but the trend was for masking to reduce the chrome uptake, again average figures are:-

3.51% $Cr_2O_3$ for the unmasked tannage
and 3.37% $Cr_2O_3$ for the masked tannage.

Finally, the duration of retannage had an over-all effect on reducing the chrome-content which was more pronounced in the case of the 50% basic than the 33% basic chrome tannage. This is shown in the 2-way table below:-

| | 1 h. in retan | 6 h. in retan | Mean |
|---|---|---|---|
| 33% basic chrome | 3.47 | 3.39 | 3.43 |
| 50% basic chrome | 3.70 | 3.19 | 3.44 |
| Mean | 3.58 | 3.29 | 3.43 |

These results indicate that some reversing of the chrome tannage takes place during retanning and that this is most pronounced in the case of the 50% basic tannage.

## Physical Testing of the Leather

### Lastometer Tests - Load at Grain Crack

Two factors were shown to be significant by the results of these tests. Firstly, the superiority of the 33% basic tannage has been confirmed as the following average results show:-

33% basic chrome-liquor, average load at grain crack 949 lb./in.

50% basic chrome-liquor, average load at grain crack 791 lb./in.

Secondly, the duration of retannage had a significant effect on the grain strength, which was affected adversely by prolonged drumming times; the mean results were:-

1 h. re-tanning time - average load at grain crack 943 lb./in.

6 h. re-tanning time - average load at grain crack 797 lb./in.

The former point is particularly interesting since Shuttleworth [3] in a report on current European practice, pointed out that whilst the tendency for high basicity tannages for full chrome leather was continuing, a preference was noted for lower basicity chrome tannage prior to retanning.

### Buckle Tear Loads

Samples were tested for strength as measured by the buckle tear test at 3 stages; i) soon after manufacture, ii) after natural ageing for 4 months, iii) after a period of artificial ageing at elevated temperature and humidity which was roughly equivalent to 1 year's storage under normal conditions. A number of factors were found to have an effect on the buckle tear strength, although no interactions were found to be highly significant.

If the conditions of the chrome tannage are considered first, only the amount of $Cr_2O_3$ offered had a significant effect on the original leather, subsequently the differences ceased to be significant. The average strength values for this factor at the three time intervals follows:-

Buckle Tear Strength (lb./in.)

| | After Manufacture | Natural Ageing | Artificial Ageing |
|---|---|---|---|
| 1.25% $Cr_2O_3$ offered | 489 | 422 | 374 |
| 2.0% $Cr_2O_3$ offered | 440 | 399 | 360 |

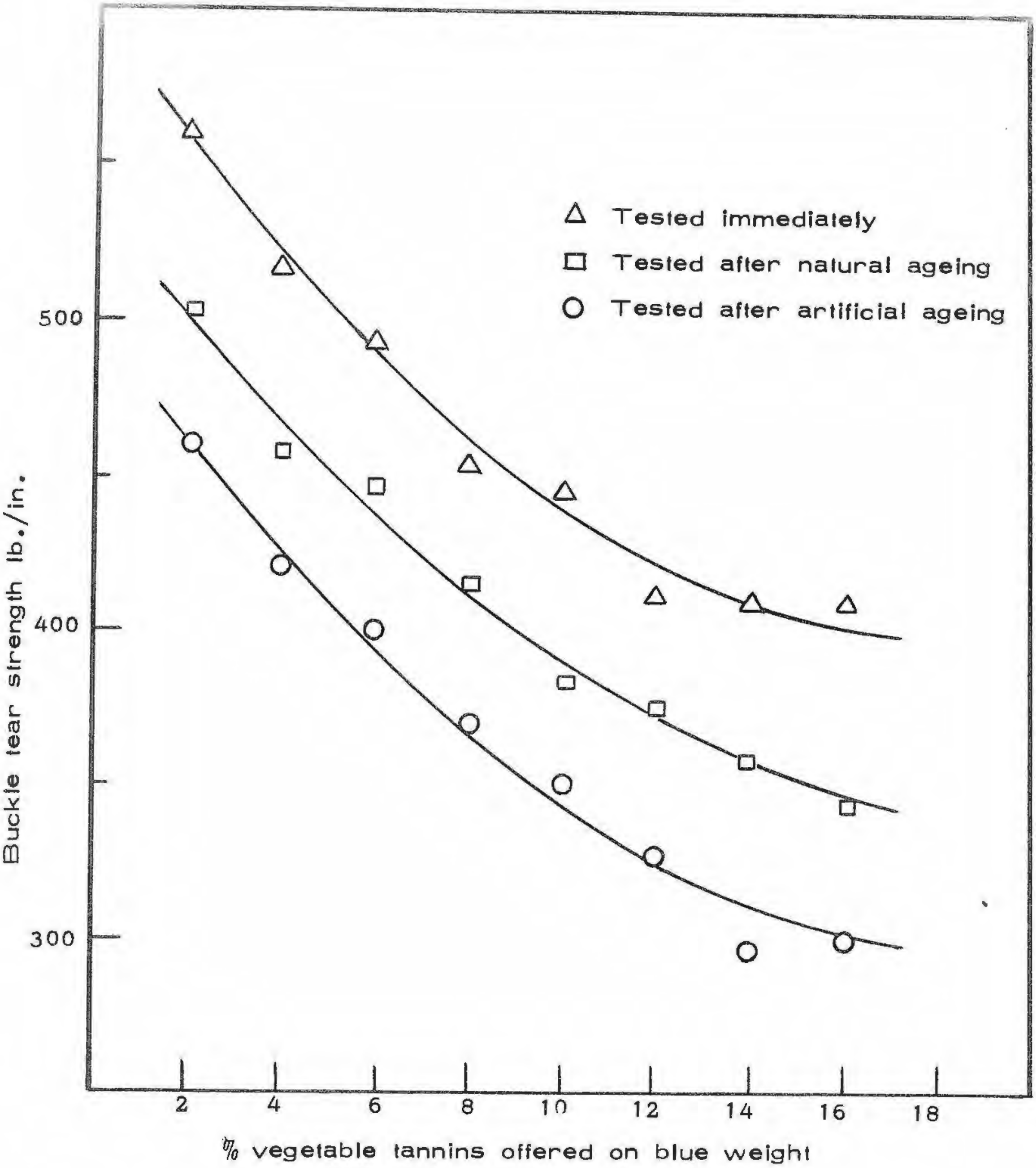


Fig. 1. Variation in strength of chrome-retan leather with degree of retannage

Whilst low basicity and masking both showed marked trends towards improving buckle tear strength, the differences between the two sets of levels used in this experiment were insufficient to show up as significantly different.

The amount of vegetable extract offered has a marked effect on the buckle tear strength and as might be expected, increased degrees of retannage brought about greater reductions in strength. The actual figures are quoted below and are also depicted graphically in Fig. 1.

Buckle Tear Strength (lb./in.)

| Amount of Wattle Extract Offered | After Manufacture | Naturally Aged | Artificially Aged |
|---|---|---|---|
| 2% tans on blue wt. | 559 | 502 | 459 |
| 4% " | 517 | 456 | 420 |
| 6% " | 515 | 449 | 390 |
| 8% " | 452 | 417 | 369 |
| 10% " | 446 | 383 | 368 |
| 12% " | 403 | 379 | 330 |
| 14% " | 410 | 360 | 296 |
| 16% " | 410 | 345 | 301 |
| Mean | 464 | 411 | 366 |

These results indicate that with up to 10% vegetable tans offered there is a progressive decrease in buckle tear strength but that after that there is little further decline in strength in the range of retannage studied. Ageing indicates that there are only minor differences in the rate of deterioration with increasing degrees of retannage.

Both the concentration of extract solution and the time of retannage bring about significant differences in the buckle tear strength, which are maintained after ageing. Average figures are:-

Buckle Tear Strength (lb./in.)

| Liquor to goods ratio | After Manufacture | Naturally Aged | Artificially Aged |
|---|---|---|---|
| 50% float | 433 | 388 | 341 |
| 200% float | 495 | 434 | 391 |
| Drumming time: | | | |
| 1 h. | 502 | 436 | 398 |
| 6 h. | 426 | 386 | 335 |

Thus it would appear that for optimum strength the duration of retannage should not be unduly long. Furthermore, these results indicate that the use of a short float is deleterious to the production of maximum strength leather; this finding requires further investigation as it is contrary to the findings obtained by the B.L.M.R.A.[4].

Acidity of the Leather

The pH of a 5% aqueous extract of the various leathers was determined at the same times as the buckle tear strength. For this analytical technique, which is much more precise than any method of physical testing, much smaller differences of means were found to be significant.

Masking yielded leathers with a slightly higher pH which persisted throughout ageing:-

| | After Manufacture | Naturally Aged | Artificially Aged |
|---|---|---|---|
| Not masked | 3.91 | 3.76 | 3.61 |
| Formate masked | 4.01 | 3.84 | 3.71 |

An increase in the amount of chrome tanning salts offered also brought about a reduction in the pH of an aqueous extract.

| | After Manufacture | Naturally Aged | Artificially Aged |
|---|---|---|---|
| 1.25% $Cr_2O_3$ offered | 4.00 | 3.86 | 3.69 |
| 2.00% $Cr_2O_3$ offered | 3.92 | 3.74 | 3.63 |

Retannage also had considerable effect on the pH of the leather, both as regards the amount of extract offered and the conditions of applying it. Dealing with the latter first it is seen that a longer float yielded on the average a leather having a higher pH; this is to be expected merely from the further dilution of the acid present in the leather, details are:-

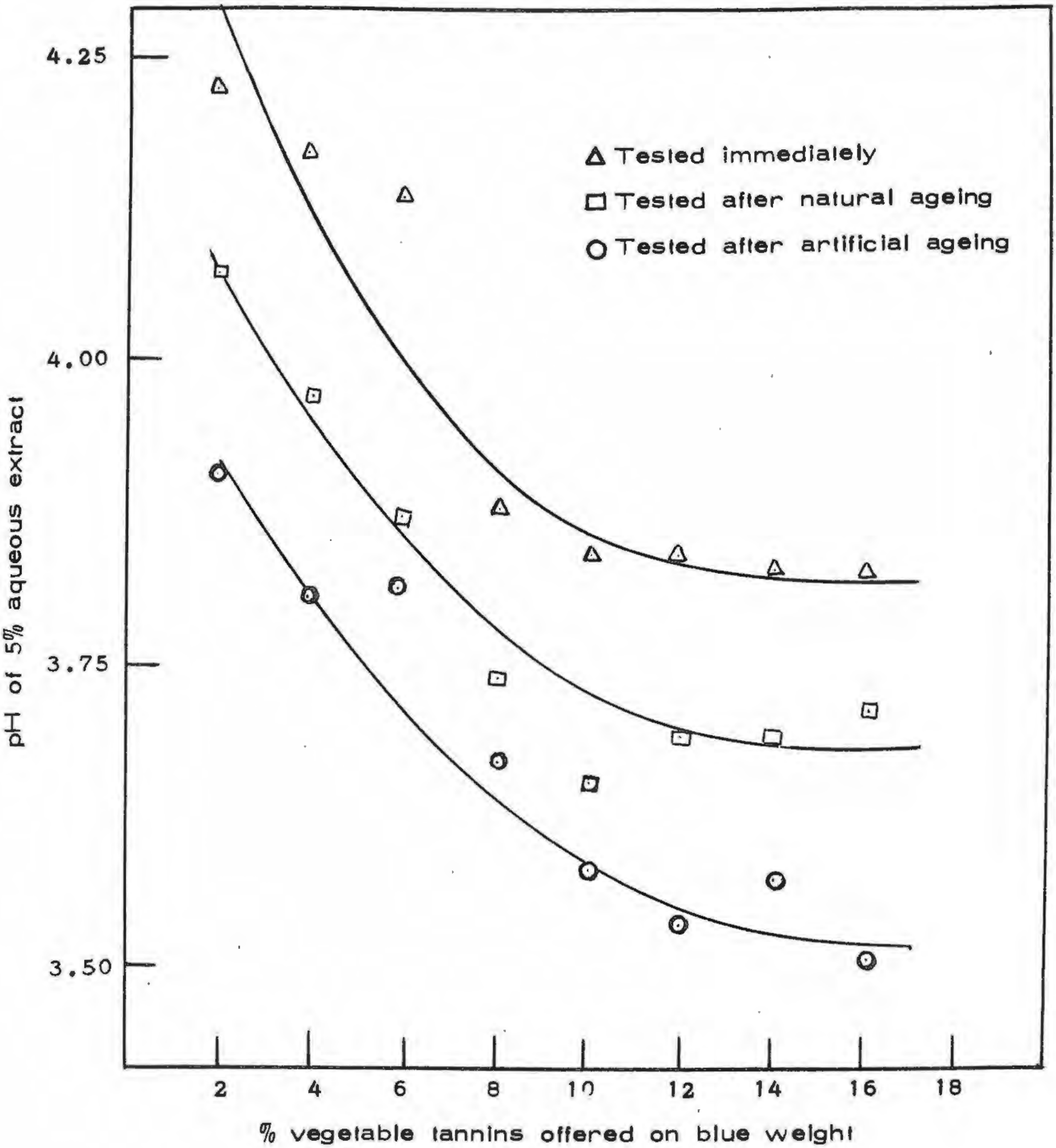


Fig. 2. The effect of the amount of vegetable tannins used in retanning on the pH of an aqueous extract of the leather.

| | After Manufacture | Naturally Aged | Artificially Aged |
|---|---|---|---|
| Retanned from 50% float | 3.85 | 3.71 | 3.57 |
| Retanned from 200% float | 4.07 | 3.89 | 3.76 |

Extension of the retannage time also brought about changes in the pH of an aqueous extract. The figures given below show that a more acid leather was produced as the retannage time was extended, this indicates that sulphate groups are replaced in the chrome complex by the polyphenolics.

| | After Manufacture | Naturally Aged | Artificially Aged |
|---|---|---|---|
| Retanned for 1 h. | 4.06 | 3.87 | 3.75 |
| Retanned for 6 h. | 3.85 | 3.73 | 3.59 |

It is most interesting to note how the pH of a 5% aqueous extract is dependent on the amount of vegetable tannins used for retanning. The mean results are quoted below and also reproduced graphically in Fig. 2.

| Amount of Vegetable Extract Offered | After Manufacture | Naturally Aged | Artificially Aged |
|---|---|---|---|
| 2% on blue wt. | 4.22 | 4.08 | 3.91 |
| 4% " | 4.17 | 3.97 | 3.80 |
| 6% " | 4.13 | 3.87 | 3.81 |
| 8% " | 3.88 | 3.74 | 3.66 |
| 10% " | 3.84 | 3.65 | 3.58 |
| 12% " | 3.84 | 3.69 | 3.53 |
| 14% " | 3.83 | 3.69 | 3.57 |
| 16% " | 3.83 | 3.71 | 3.50 |

The three curves shown in Fig. 2 show a marked similarity to those shown in Fig. 1 where the buckle tear strength was plotted against the amount of vegetable extract offered. This indicates that the buckle tear strength may be a function of the pH of the leather. Accordingly a plot of pH of aqueous extract against buckle tear strength has been made and is shown in Fig. 3. The general trend of this relationship is linear and it seems that a higher pH of aqueous extract gives rise to a stronger leather.

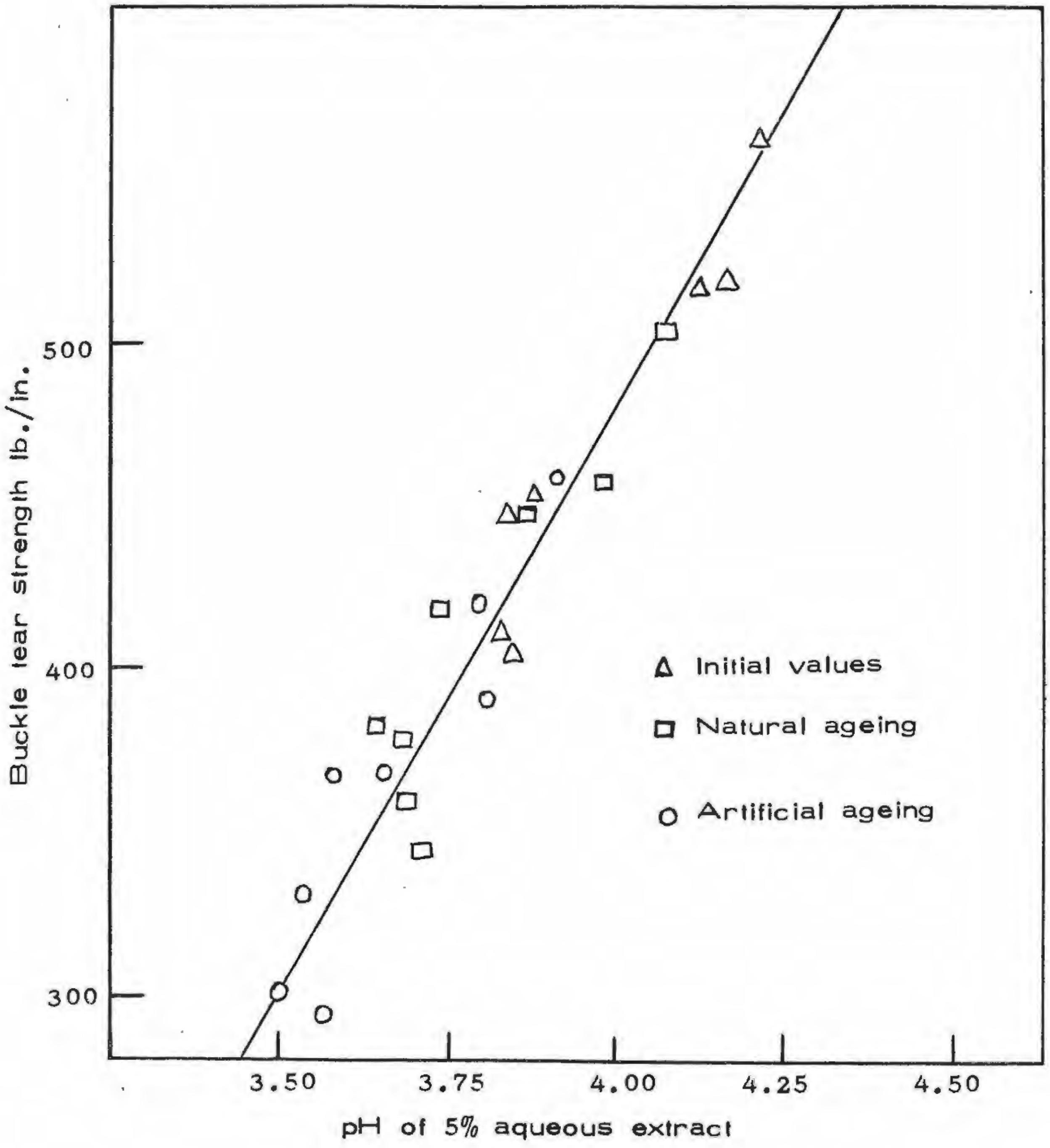


Fig. 3. Relation between pH of aqueous extract and tearing strength of chrome-retan leathers.

## DISCUSSION OF RESULTS

The discussion of results may conveniently be divided into two parts.

The first dealing with the preparation of the chrome stock indicates that the use of a low amount of chrome tanning salts gives rise to a somewhat stronger leather after subsequent retanning. Chemical analysis indicates that the utilisation of the chrome is more efficient when the lower amount is offered. As found in a previous experiment the basicity of the chrome tannage has an effect on the strength after retanning, and tannage with 33% basic salts is preferable, particularly for high grain strength. Chemical analysis indicated that some de-chroming takes place during retanning and that this is most pronounced for the 50% basic tannage, although the lower chrome content of the leather may be a function of increased fixation of tannin. Formate masking had no statistically significant effect on the leather strength although the trend was towards slightly improved strength in the masked leathers. There was no indication that masking reduced the rate of deterioration of the leather.

Consideration of the retannage showed that there was a progressive decline in strength with increasing amounts of retannage but that there was a tendency for this to level off at about the 12% level. The rate of deterioration on storage seems to be about the same irrespective of the amount of vegetable extract used for retanning. Unfortunately, full-chrome leathers were not included in this experiment, but extrapolation indicates that some deterioration in the strength of a full-chrome leather would be likely.

The conditions of retannage are important, particularly the length of time which the chrome leather stays in the retanning drum. However, it must be remembered that in these experimental tannages fatliquoring and drying were carried out immediately after retanning. In practice, it is unlikely that this would happen, and there remains the possibility that changes bringing about loss of strength may occur while the leather is horsed as well as while it is in the drum. This point is being investigated at the present time, but in the interim it can be suggested that a short time in the retan drum, followed by fatliquoring and drying with the minimum delay will be conducive to optimum strength. Rather surprisingly application of the wattle extract from concentrated solution produced a weaker leather than when a long float was used. Since these retannages were carried out in small drums it is unlikely that the weakness was due to mechanical action, but rather that the effect is chemical. As has already been stated, this finding is contrary to that of the B.L.M.R.A. and it is intended to obtain further information on this in future experiments.

Finally, mention must be made of the relationship which was shown in Fig. 3 between the pH of an aqueous extract of the leather and the buckle tear strength. Whilst this is interesting, undue stress must not be placed on this finding since factors which only affect the mechanical properties of the leather would only alter the buckle tear strength and not the pH of a leather extract. Thus a greatly improved liming method, or an intrinsically better hide would displace the graph upwards without altering the slope. However, the generalisation that for a given type of tannage the physical strength is related to the pH seems reasonable within the range of values found in this work. The fact that on ageing the decreases in both pH and physical strength are proportional indicates that acidity plays some part in the mechanism of the reaction.

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# R.B. 355. COMPARISON OF VEGETABLE TANNING EXTRACTS FOR RETANNING CHROME-TANNED PELT

by

D.A. Williams-Wynn and R. Dalling.

## SUMMARY

A comparative study has been undertaken of the effects of five commercially available vegetable tanning extracts, wattle, chestnut, myrobalans, myrtan and quebracho, in the manufacture of chrome-retan leather. The vegetable tannins were offered to blue leather tanned with two levels of chromium after neutralising with either sodium bicarbonate or alkaline polyphosphate. The leathers were assessed for thickness, stiffness, shrinkage temperature, lastometer load and extension at grain crack, tensile strength and slit tear strength.

The greatest degree of plumpness was given by wattle and quebracho and the least by myrobalans; the best lastometer figures were obtained using wattle and myrobalans, and the highest tensile and tearing strengths were given by myrtan. Thus it is obvious that no one extract is superior in every respect and the choice of extract will depend on the effect desired. The relative positions for each extract are given in the accompanying table.

| | Wattle | Chestnut | Myrobalans | Myrtan | Quebracho |
|---|---|---|---|---|---|
| Shrinkage Temp. | 2 | 4 | 5 | 3 | 1 |
| Plumpness | 1 | 3 | 5 | 4 | 1 |
| Lastometer Load | 2 | 4 | 1 | 3 | 5 |
| Lastometer Extn. | 1 | 5 | 2 | 2 | 4 |
| Tensile Strength | 2 | 3 | 4 | 1 | 5 |
| Slit Tear Strength | 3 | 4 | 2 | 1 | 5 |

The level of chrome tannage was relatively unimportant but there was evidence that lower strength characteristics were obtained when the higher chrome level was used, especially with wattle and quebracho retanned leathers. Neutralising with alkaline polymeric phosphate has resulted in considerable improvements in many of the physical properties of the leathers, the effect being particularly marked in those leathers retanned with wattle, myrtan and quebracho.

## INTRODUCTION

Chrome tanned leathers have very different characteristics from vegetable tanned leathers, the former being noted for their springiness and high hydrothermal stability, whereas vegetable tanned leathers are full and tight. It was inevitable that combinations of the two types of tannage should have been attempted in the hope that the resulting leather would have the better properties of both. To some extent this has been achieved, but some properties have had to be compromised. Thus lightly retanned leathers possess the springiness of full-chrome leathers but with improved tightness especially in the flanks. On the other hand, heavily retanned leathers approach vegetable tanned leathers having a fullness and roundness associated with these leathers, but with improved hydrothermal stability.

In the early stages of development of the combination tannage many tanners experienced considerable difficulty in producing satisfactory leather which also had good ageing characteristics. All of the commercially available vegetable tanning materials were tried for retanning but all suffered from the disadvantage of producing unstable leather when used injudiciously. Whilst the mechanism of the deterioration is still imperfectly understood, considerable information on the manufacture and properties of chrome-retan leathers has been published [1-4]. Most of this information was obtained from experiments involving the use of wattle extract for retanning. A comprehensive range of vegetable tanning materials was used in a comparative study of their use for retanning and the results were given in a recent publication [5]. The leathers were prepared according to current American practice of heavy retannage, and are therefore not of direct local interest. The results reported here are based on relatively lightly retanned leathers produced using a limited range of vegetable tanning extracts.

## EXPERIMENTAL

### Plan of the Experiment

Only three factors were varied, the type of vegetable tanning extract, the level of chrome tannage and the type of neutralisation of the chrome tanned pelt, as detailed below. The results were analysed statistically.

A Vegetable Tanning Material

- A1 Wattle
- A2 Chestnut
- A3 Myrobalans
- A4 Myrtan
- A5 Quebracho

B Level of Chrome Tannage

- B1 1% $Cr_2O_3$ on limed weight
- B2 2% $Cr_2O_3$ on limed weight

C Type of Neutralising Agent

- C1 1% sodium bicarbonate
- C2 1% polyphosphate plus 0.5% sodium bicarbonate

<u>Preparation of the Leathers</u>

A hide limed for upper leather was split in lime to give a final leather thickness of approximately 2 mm. Forty rectangles were cut from the butt area of the limed pelt and numbered and the above treatments allocated at random.

All the pelt pieces were washed in running water, then floated in 400% of water at 35°C, and 1.5% of ammonium sulphate added in two portions at 10 min. interval. Deliming was continued for 30 min., when 1% of a pancreatic enzyme bate was added and the drum run for a further 30 min. The delimed pelt was sorted into two groups according to factor B and each was pickled with 5% salt and 0.6% sulphuric acid in 100% water for 1 hour. To the exhausted pickle liquor was added either 1% $Cr_2O_3$ or 2% $Cr_2O_3$ as the 33% basic chrome tanning salt dissolved in about 20% of water. Drumming was continued for 4 hours and the goods were left in the liquor over-night. The following morning the pH of the chrome liquor was adjusted to 3.7 over a period of 4 hours by the addition of sodium bicarbonate. The blue leather was horsed for several days before going forward for neutralising and retanning.

After samming and setting out, the chrome tanned pieces were sorted for factor C. To the leather in 100% water was added either 1% sodium bicarbonate or 1% polyphosphate plus 0.5% sodium bicarbonate and neutralising continued for 1 hour. The liquor was drained off then the leather was washed for 10 min. in running water before sorting for factor A.

Retannage was effected in 100% float, the quantity of the vegetable extracts offered being calculated on 5% tans in each case. After retanning for 1 hour the leathers were washed first cold, then in water at 50°C and fatliquored in a 50% float for 40 min. offering 1.5% sulphated neatsfoot oil and 1.5% raw neatsfoot oil. The leathers were piled over-night, pasted to dry, damped back, staked and plated.

The leathers were assessed for shrinkage temperature, thickness and stiffness as well as the usual physical properties.

## RESULTS

### Composition of the Vegetable Tanning Extracts

Wattle Extract

| | |
|---|---|
| Tannins | 61.7% |
| Non-tannins | 19.1% |
| Insolubles | 0.4% |
| Moisture | 18.8% |
| Tan/Non-tan Ratio | 3.23 |

Chestnut Extract

| | |
|---|---|
| Tannins | 57.9% |
| Non-tannins | 29.5% |
| Insolubles | 2.0% |
| Moisture | 10.6% |
| Tan/Non-tan Ratio | 1.96 |

Myrobalans Extract

| | |
|---|---|
| Tannins | 55.3% |
| Non-tannins | 28.8% |
| Insolubles | 5.2% |
| Moisture | 10.7% |
| Tan/Non-tan Ratio | 1.92 |

Myrtan Extract

| | |
|---|---|
| Tannins | 63.2% |
| Non-tannins | 25.6% |
| Insolubles | 3.5% |
| Moisture | 7.7% |
| Tan/Non-tan Ratio | 2.47 |

Quebracho Extract (Sulphited)

| | |
|---|---|
| Tannins | 69.4% |
| Non-tannins | 14.6% |
| Insolubles | 1.4% |
| Moisture | 14.6% |
| Tan/Non-tan Ratio | 4.77 |

Shrinkage Temperature

The shrinkage temperature was determined by heating the wet leather strips in liquid paraffin since the majority of the leathers stood the boil. The figures for the various treatments are given in Table I.

Table I
Shrinkage Temperature

| | | Vegetable Tannin | | | | | Mean |
|---|---|---|---|---|---|---|---|
| | | Wattle | Chest. | Myrob. | Myrtan | Queb. | |
| bicarbonate neutralisation | 1% $Cr_2O_3$ | 95 | 92 | 89 | 94 | 100 | 94.2 |
| | 2% $Cr_2O_3$ | 104 | 101 | 98 | 101 | 104 | 102.1 |
| | Mean | 100 | 97 | 94 | 98 | 102 | 98.2 |
| phosphate neutralisation | 1% $Cr_2O_3$ | 93 | 93 | 89 | 92 | 95 | 92.4 |
| | 2% $Cr_2O_3$ | 103 | 99 | 98 | 102 | 104 | 101.6 |
| | Mean | 98 | 96 | 94 | 97 | 100 | 97.0 |

It is obvious that factor B, the level of chrome tannage, is very important, the higher level of chrome giving a higher shrinkage temperature. Also very important is the type of retanning material, wattle and quebracho extracts giving substantially higher shrinkage temperatures than the other extracts; myrobalans on the other hand has resulted in considerably lower shrinkage temperatures.

An interesting result is due to the type of neutralising material used. Although the difference between the two neutralising agents, sodium bicarbonate and an alkaline polyphosphate, is small, the phosphate neutralising has resulted in lower shrinkage temperatures in each case.

Thickness

The average thickness over the area of each leather sample was calculated from the thickness measurements of the test specimens. The result of this assessment is given in Table II.

Table II
Thickness mm.

| | | Vegetable Tannin | | | | | |
|---|---|---|---|---|---|---|---|
| | | Wattle | Chest. | Myrob. | Myrtan | Queb. | Mean |
| bicarbonate neutralisation | 1% $Cr_2O_3$<br>2% $Cr_2O_3$ | 2.4<br>2.2 | 2.5<br>2.2 | 1.9<br>2.3 | 2.3<br>2.1 | 2.4<br>2.4 | 2.3<br>2.2 |
| | Mean | 2.3 | 2.4 | 2.1 | 2.2 | 2.4 | 2.3 |
| phosphate neutralisation | 1% $Cr_2O_3$<br>2% $Cr_2O_3$ | 2.4<br>2.6 | 2.3<br>2.2 | 1.9<br>2.1 | 2.3<br>2.1 | 2.6<br>2.2 | 2.3<br>2.2 |
| | Mean | 2.5 | 2.3 | 2.0 | 2.2 | 2.4 | 2.3 |

Only the type of vegetable retanning material significantly influenced the thickness of the leathers. From the results in the above table it is obvious that wattle and quebracho gave the plumpest leather, whereas the myrobalans retannage resulted in the least plumping. The difference between 2.0 mm. and 2.4 mm. is likely to be of economic importance if plumping and filling is the main feature.

Neither of the other factors had an important influence on the thickness.

Stiffness

The leathers were assessed manually for stiffness, scores being allocated on the basis 0, soft and flexible to 4, firm. The results of this assessment are given in Table III.

Table III
Stiffness (high, firm)

| | | Vegetable Tannin | | | | | |
|---|---|---|---|---|---|---|---|
| | | Wattle | Chest. | Myrob. | Myrtan | Queb. | Total |
| bicarbonate neutralisation | 1% $Cr_2O_3$<br>2% $Cr_2O_3$ | 3<br>3 | 7<br>2 | 3<br>0 | 5<br>0 | 4<br>1 | 22<br>6 |
| | Total | 6 | 9 | 3 | 5 | 5 | 28 |
| phosphate neutralisation | 1% $Cr_2O_3$<br>2% $Cr_2O_3$ | 4<br>2 | 7<br>2 | 3<br>1 | 7<br>1 | 5<br>2 | 26<br>8 |
| | Total | 6 | 9 | 4 | 8 | 7 | 34 |

The most important factor in controlling the stiffness was the level of chrome tannage: the greater the amount of chromium offered, the softer the leather. The type of retanning material is also important, very large differences being noted between the myrobalans retanned leather which was soft, and the chestnut retanned leather which was firm. Myrtan, wattle and quebracho retanned leathers were similar and moderately flexible. There was no significant difference between the neutralising treatments although there was a trend indicating increased firmness due to the phosphate neutralising.

<u>Lastometer Load at Grain Crack</u>

The load at grain crack was determined in the usual manner and the results given in Table IV are calculated to lb./in. thickness.

Table IV
<u>Lastometer Load (lb./in.)</u>

| | | Vegetable Tannin | | | | | Mean |
|---|---|---|---|---|---|---|---|
| | | Wattle | Chest. | Myrob. | Myrtan | Queb. | |
| bicarbonate neutralisation | 1% $Cr_2O_3$<br>2% $Cr_2O_3$ | 1407<br>1004 | 848<br>764 | 1263<br>1201 | 1243<br>1254 | 811<br>618 | 1115<br>968 |
| | Mean | 1205 | 806 | 1232 | 1248 | 715 | 1042 |
| phosphate neutralisation | 1% $Cr_2O_3$<br>2% $Cr_2O_3$ | 1569<br>1253 | 1525<br>1118 | 1425<br>1431 | 1060<br>1165 | 1123<br>1333 | 1341<br>1260 |
| | Mean | 1411 | 1321 | 1428 | 1113 | 1228 | 1300 |

It is obvious that the most important factor affecting the load at grain crack is the type of neutralisation. The use of alkaline phosphate has resulted in a considerable increase in the grain strength of the leather, an increase of almost 30%. This effect is evident in all leathers except those retanned with myrtan.

Of the vegetable tanning materials, myrobalans resulted in the strongest leather followed closely by wattle. The weakest leather was given by myrtan and quebracho, but if only those leathers neutralised with the bicarbonate are considered, very low strengths were found for chestnut and quebracho.

The level of chrome tannage is relatively unimportant and only with wattle, chestnut and to a lesser extent quebracho does the high level of chrome cause lower grain strength.

Lastometer Extension at Grain Crack

The grain extension at crack is recorded in Table V.

Table V
Lastometer Extension (mm.)

| | | Vegetable Tannin | | | | | |
|---|---|---|---|---|---|---|---|
| | | Wattle | Chest. | Myrob. | Myrtan | Queb. | Mean |
| bicarbonate neutralisation | 1% $Cr_2O_3$<br>2% $Cr_2O_3$ | 8.8<br>7.8 | 6.5<br>6.9 | 7.7<br>8.1 | 8.6<br>9.1 | 8.4<br>7.2 | 8.0<br>7.9 |
| | Mean | 8.3 | 6.7 | 7.9 | 8.9 | 7.9 | 7.9 |
| phosphate neutralisation | 1% $Cr_2O_3$<br>2% $Cr_2O_3$ | 10.1<br>8.6 | 7.9<br>7.6 | 9.1<br>9.3 | 7.1<br>9.3 | 9.2<br>8.4 | 8.7<br>8.6 |
| | Mean | 9.3 | 7.7 | 9.2 | 8.2 | 8.8 | 8.7 |

Retannage with chestnut extract has resulted in the lowest extension at grain crack, especially in those leathers given a normal bicarbonate neutralisation. The greatest extensibility was given by wattle and myrobalans.

The introduction of phosphate during the neutralisation has resulted in improved grain extension in each case except the myrtan retannage. The level of chrome tannage was unimportant except in the case of wattle and quebracho where the higher level of chrome has produced less extensible leather.

Tensile Strength

Tensile strength was determined parallel to the backbone. The average results for this determination are given in Table VI.

Table VI

Tensile Strength (lb./sq.in.)

| | | Vegetable Tannin | | | | | Mean |
|---|---|---|---|---|---|---|---|
| | | Wattle | Chest. | Myrob. | Myrtan | Queb. | |
| bicarbonate neutralisation | 1% $Cr_2O_3$<br>2% $Cr_2O_3$ | 2150<br>2950 | 2380<br>3010 | 2930<br>2240 | 2570<br>2290 | 2470<br>1500 | 2500<br>2400 |
| | Mean | 2550 | 2700 | 2590 | 2430 | 1980 | 2450 |
| phosphate neutralisation | 1% $Cr_2O_3$<br>2% $Cr_2O_3$ | 2940<br>3080 | 2720<br>2520 | 2860<br>2210 | 3310<br>3560 | 2400<br>2850 | 2850<br>2850 |
| | Mean | 3010 | 2620 | 2540 | 3440 | 2630 | 2850 |

Due to the very variable nature of the results none of the factors had a significant influence at the 5% level. However, there is strong evidence that incorporation of phosphate during the neutralisation had resulted in substantially increased strength.

There is no doubt that myrtan and wattle give leather with a high tensile strength especially if the leather had been pretreated with phosphate in the neutralising.

Slit Tear Strength

The results for the determination of slit tear strength are given in Table VII.

Table VII

Slit Tear Strength (lb./in.)

| | | Vegetable Tannin | | | | | Mean |
|---|---|---|---|---|---|---|---|
| | | Wattle | Chest. | Myrob. | Myrtan | Queb. | |
| bicarbonate neutralisation | 1% $Cr_2O_3$<br>2% $Cr_2O_3$ | 797<br>590 | 633<br>586 | 716<br>684 | 901<br>606 | 547<br>526 | 719<br>598 |
| | Mean | 694 | 610 | 700 | 753 | 537 | 659 |
| phosphate neutralisation | 1% $Cr_2O_3$<br>2% $Cr_2O_3$ | 781<br>645 | 638<br>720 | 714<br>737 | 994<br>960 | 775<br>603 | 780<br>733 |
| | Mean | 713 | 679 | 726 | 977 | 689 | 759 |

The type of vegetable tannin used for retanning had a very considerable influence on the strength of the leather. Myrtan resulted in leather with the highest strength, myrobalans and wattle were similar in effect and produced leather of about average strength, but chestnut and quebracho gave leather with rather low tearing strength.

Neutralising was also very important, the alkaline phosphate resulting in a considerable increase in strength compared with the normal bicarbonate neutralisation. The effect of the level of chrome tannage was not significant at the 5% level, but there was a trend which indicated that the higher chrome content resulted in a lower tearing strength.

## DISCUSSION AND CONCLUSIONS

The type of retanning agent has had a considerable influence on the properties of the leather. The highest shrinkage temperatures were given by wattle and chestnut, and the lowest by myrobalans; the leather with the greatest plumpness was given by wattle and quebracho, and the least by myrobalans; chestnut resulted in the greatest stiffness and myrobalans gave the softest leather; greatest grain strength was given by myrobalans and wattle, and the lowest by chestnut and quebracho; the most extensible leather was given by wattle and myrobalans, and the least extensible by chestnut; myrtan gave leather with the highest tensile strength, whilst the leather with the lowest tensile strength was produced by retanning with myrobalans and quebracho; myrtan gave leather with the highest tearing strength, whereas quebracho and chestnut tended to give rather low tearing strengths. Thus it is obvious that there is no one vegetable tanning extract which is superior in all respects to the others. Therefore the choice of extract will depend on the quality desired, but care will have to be exercised not to sacrifice other properties merely to attain the maximum of any given effect. Wattle tannin, which is of particular interest to South African leather manufacturers because of its availability and cheapness, gives maximum plumpness without seriously affecting the other properties of the leather, and since increasing the thickness is one of the main reasons for retanning, this tannin is of particular value.

The level of chrome tannage did not influence the results for the different vegetable tanning materials equally. The greater quantity of chromium tended to reduce the strength and extensibility of the wattle and quebracho retanned leathers but had a smaller influence on the other tanning materials, although the results for tensile strength must not be considered because of their erratic nature. The higher chrome content has resulted in higher shrinkage temperatures and greater softness, but has not seriously affected the other properties.

The incorporation of polymeric phosphate in the neutralising resulted in considerable improvements in many of the physical properties of the chrome-retan leathers. Not all of the vegetable tanning extracts behaved similarly, the use of phosphate being beneficial mainly in those leathers retanned with wattle, myrtan and quebracho. This confirms results of previous work in which phosphates were investigated for pre-retan treatments of wattle retanned leather[6] when the strength characteristics were significantly improved.

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# R.B. 421. THE ASTRINGENCY OF VEGETABLE TANNING EXTRACTS FOR RETANNING

by

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## SUMMARY

The effects of a variety of different vegetable tanning extracts on the properties of retan upper leather have been reviewed, and a study of the affinity of several of the more important commercially available extracts has been made. The uptake of extract from an excess of vegetable tan solution by chrome tanned hide substance and by pelt pieces was determined, and thickness measured. The effect of retanning on the chrome content and on pH has also been assessed.

In terms of weight increase, chestnut was the most effective although by suitable adjustment of conditions wattle and quebracho are equally effective, and these give the greatest plumping and thickness increase whilst chestnut is inferior. Sulphited wattle is not an effective retanning agent since plumping is reduced and the two sulphited extracts were the most effective in stripping chromium. No chromium was solubilised by chestnut, wattle or myrtan. Chestnut and myrtan resulted in low pH values.

The type of neutralisation also affected the results, although only the polymeric phosphate significantly reduced the uptake of vegetable tannin but had no effect on the substance of the leather. The three neutralising agents, sodium sulphite, neutral syntan and polymeric phosphate, were less effective than calcium formate and sodium bicarbonate for reducing the acidity of the system and tended to cause greater chrome solution.

It is evident that wattle and quebracho are the most effective for use in retanning, but care must be exercised in the use of sulphited extracts because of their greater reactivity with chromium and lower affinity for the pelt.

## INTRODUCTION

The practical and theoretical implications of the retannage of chrome leather with vegetable tannins have been extensively reviewed[1-3]. Nevertheless, not many comparative studies of the effect of different vegetable tanning materials have been made in recent years and of these only a few are based on scientific principles and from which valid conclusions can be

Note: 1, refers to the vegetable tanning extracts which have resulted in the best physical properties, have given the highest shrinkage temperature and have stripped least chrome.

2, refers to those which have given the poorest physical properties, lowest shrinkage temperature and greatest chrome stripping.

Although the effect of retanning on chrome stripping and on shrinkage temperature may be important in determining durability and stability of tannage, the more important reason for retanning is for filling and improving the substance of the leather, yet maintaining satisfactory physical characteristics. There is no doubt that wattle and quebracho fulfil the first of these requirements[4,8], and are superior to other extracts in this respect. Moreover, these same authors agree that myrobalans gives the poorest filling and plumping effect.

There is some disagreement as far as grain crack and tearing strength are concerned. For best grain crack results Stubbings[8] claims sumac and quebracho to be superior, the least satisfactory being chestnut and wattle. Williams-Wynn[4] has found that wattle and myrobalans are the best, and the poorest results are given by chestnut and quebracho. Whilst these authors agree that chestnut is not satisfactory for producing a strong elastic grain, one [8] claimed that quebracho is best and wattle worst, whereas the other [4] found the exact opposite. The explanation of this difference of opinion probably lies in the fact that Stubbings used conditions of retanning which are known to be satisfactory for quebracho and which may not necessarily have suited other vegetable tanning extracts.

As shown in the table, myrtan was found to give leather with the greatest tearing strength and quebracho the weakest leather. On the other hand, in one case wattle was found to give results almost equal to myrtan, whereas in the other, wattle is claimed to be no better than quebracho.

These apparently contradictory results are probably caused by different requirements in the two countries concerned, the most important factor being the level of retannage used. In the United States heavy retannages are common and in the experimental work quoted above all formulae including temperatures and floats were those in common use in tanneries. The techniques of retanning used in these laboratories were geared to the requirements of European leather manufacturers who demand relatively light retannages because the "vegetable" character in upper leather is regarded as undesirable. It is not surprising therefore that differences of opinion have arisen.

One aspect of the retannage of chrome leather with vegetable tannins which seems to have been overlooked is the astringency of the various extracts. Kanagy[9] has attempted to measure the uptake of tanning material by chrome tanned pelt but there has been some criticism of his work by Gustavson[11] who claimed that the analytical approach that had been used was subject to error. Certainly the Kubelka[13] factor of 2.73 for converting chromic oxide content to "chrome tannin" is not accurate[11,12] and hence the assessment of vegetable tan by difference will also be in error. Probably the only satisfactory method for determining the vegetable tan content in experimental leathers is to determine the weight increase of the retanned leathers compared with a blank. This is the method used in the present work but the results cannot be regarded as absolute because displacement of sulphate and/or chromium is not taken into account.

The object of the present investigation was to determine the amounts of the various vegetable tanning extracts taken up by chrome tanned hide substance after neutralisation with a variety of basic materials and the influence on substance and other properties. Details of the variables and of the tanning technique are given in the following section.

## EXPERIMENTAL

### Factors Varied

A Level of chrome tannage

- A1 low, 1% $Cr_2O_3$ offered on limed weight
- A2 medium, 2% $Cr_2O_3$ offered on limed weight.

B Neutralising material

- B1 calcium formate, 1% on blue weight
- B2 sodium bicarbonate, 1% on blue weight
- B3 sodium sulphite, 1% on blue weight
- B4 neutral syntan, 1% on blue weight
- B5 polymeric phosphate, 1½% on blue weight.

C Vegetable tanning extract

- C1 wattle
- C2 quebracho (sulphited)
- C3 chestnut (sweetened)
- C4 wattle (sulphited)
- C5 myrtan
- C6 control.

Tanning Technique

Standard hide powder (batch No. C.22) and calf skin squares were used as the substrate. Limed calfskin, split to a uniform substance was cut into the requisite number of 3 in. x 4 in. rectangles, delimed with 1% boric acid, bated, washed and scudded. Portions of hide powder, previously wet with water, were added at this stage, allowance being made for the extra material assuming 25% hide substance in limed pelt. All pickling and subsequent tanning processes were performed in glass Wacker drums.

Because of the presence of bulky hide powder, pickling (and chrome tanning) were performed in a 250% float of 6% salt to which was added 0.5% of sulphuric acid on estimated limed weight. After drumming for 1 hour, the requisite quantity of 33% basic chrome tanning salt was added dissolved in 25% of water. During the tannage the temperature was raised to 45°C over 4 hours and maintained at that temperature for a total of 6 hours. The pelt was left in the liquor over-night, tumbled for 1 hour and drained. The hide powder was separated from the pelt pieces, squeezed to express the liquid and washed once with distilled water. The chrome tanned hide powder was squeezed to a standard moisture content, well mixed and equal amounts were transferred to shaker bottles for neutralising and retanning. The pelt pieces were squeezed and washed, and added to the hide powder in the shaker bottles.

Sufficient water was added to each of the bottles to ensure a fluid slurry of hide powder when the requisite quantity of neutralising material was added. The goods were agitated at 60 r.p.m. for 1 hour when they were drained, squeezed to express excess moisture and returned to the shaker bottles.

Water was added to the neutralised goods in sufficient quantity to ensure that together with the large excess of vegetable tanning extract solution, enough liquid was present to make a slurry. The hide powder and pelt pieces were tumbled in the solution of vegetable extract (200% solids on blue weight) for 24 hours, when the liquor was drained off and the goods washed in 2 changes of distilled water to remove loosely combined and soluble solids. The hide powder was dried in an air oven at 50°C and the pelt pieces were vacuum dried.

## RESULTS

The dried hide powder was weighed to determine percentage weight increase due to retanning and then analysed for chrome on hide substance. The pelt pieces had been split to uniform substance before retanning and were measured in the dry state and the relative thickness determined. The pH of the exhaust vegetable retan liquors was also measured.

### Weight Increase, %

The weight increase due to the retannage is the most significant effect noted, but the increase in weight is dependent to some extent on the level of chrome tannage as shown by the results given below.

| | Level of Chrome Tannage | | Mean |
|---|---|---|---|
| | 1% $Cr_2O_3$ | 2% $Cr_2O_3$ | |
| Wattle | 77.7 | 86.2 | 81.9 |
| Quebracho (sulphited) | 76.4 | 85.8 | 81.1 |
| Chestnut (sweetened) | 81.4 | 85.7 | 83.6 |
| Wattle (sulphited) | 72.9 | 79.6 | 76.2 |
| Myrtan | 81.7 | 79.7 | 80.7 |
| Mean | 78.1 | 83.2 | 80.6 |

It is obvious that, at the low level of chrome tannage, chestnut and myrtan have given the greatest percentage weight increase, and sulphited wattle the least. It is significant that sulphiting, albeit at a low level, has considerably reduced the affinity of wattle extract for chrome tanned hide substance. This is equally so at the high level of chrome tannage where normally the affinity is greater. At the high level of chrome tannage wattle, quebracho and chestnut are approximately equally taken up and all show markedly increased affinity compared with the 1% level of chrome. One unusual observation was the lower uptake of myrtan by the pelt tanned with 2% of chrome compared with the 1% chrome level.

Of less significance was the type of neutralisation. Nevertheless, quite large differences in the uptake of vegetable tans was caused by variations in the neutralising material

| | Level of Chrome Tannage | | Mean |
|---|---|---|---|
| | 1% $Cr_2O_3$ | 2% $Cr_2O_3$ | |
| Calcium formate | 80.6 | 83.7 | 82.1 |
| Sodium bicarbonate | 78.5 | 82.3 | 80.4 |
| Sodium sulphite | 78.7 | 84.2 | 81.4 |
| Neutral syntan | 79.3 | 85.6 | 82.4 |
| Polymeric phosphate | 73.2 | 81.2 | 77.2 |
| Mean | 78.1 | 83.2 | 80.6 |

Although the differences were relatively small in most cases the use of polymeric phosphate has undoubtedly reduced the affinity of chrome tanned pelt for vegetable extracts. The neutral syntan has on average resulted in the greatest weight increase, probably due to the fact that the syntan was bound to the protein and did not act merely as a basifying alkali.

Thickness, mm.

The leathers that had not been retanned dried out very wrinkled and curled and an accurate assessment of the thickness of these leathers was impossible. On the other hand the retanned leathers dried out perfectly flat and these were measured, but no estimate of the increase in thickness could be obtained. Hence the results given below list the actual thickness, each the average of 8 measurements, for the various retanning materials.

| | Level of Chrome Tannage | | Mean |
|---|---|---|---|
| | 1% $Cr_2O_3$ | 2% $Cr_2O_3$ | |
| Wattle | 2.4 | 2.4 | 2.4 |
| Quebracho (sulphited) | 2.4 | 2.5 | 2.4 |
| Chestnut (sweetened) | 2.2 | 2.4 | 2.3 |
| Wattle (sulphited) | 1.9 | 2.2 | 2.1 |
| Myrtan | 2.1 | 2.3 | 2.2 |
| Mean | 2.2 | 2.4 | 2.3 |

Wattle and quebracho are equivalent in their plumping action and the value for chestnut is probably not significantly different. On the other hand, there is no doubt that sulphited wattle and myrtan have resulted in thinner leather.

The type of neutralising material had no significant influence on the thickness of the leather.

Chrome on Hide Substance, %

Because of the variable weight increases due to the tannage variables, chromium had to be determined on a hide substance basis. The effect of the various vegetable retanning materials on the chrome content is given below.

| | Level of Chrome Tannage | | Mean |
|---|---|---|---|
| | 1% $Cr_2O_3$ | 2% $Cr_2O_3$ | |
| Wattle | 2.67 | 4.30 | 3.48 |
| Quebracho (sulphited) | 2.54 | 4.06 | 3.30 |
| Chestnut (sweetened) | 2.72 | 4.31 | 3.51 |
| Wattle (sulphited) | 2.63 | 4.08 | 3.35 |
| Myrtan | 2.70 | 4.25 | 3.47 |
| No retannage | 2.72 | 4.38 | 3.55 |
| Mean | 2.66 | 4.23 | 3.44 |

The chrome content of the leathers was not greatly affected by wattle, chestnut or myrtan, but the two sulphited extracts, quebracho and sulphited wattle, have caused a significant loss of chromium particularly in the leathers pretanned with the high level of chromium.

Another interesting observation is the effect of the neutralising agents on the chrome content as shown.

| | Level of Chrome Tannage | | Mean |
|---|---|---|---|
| | 1% $Cr_2O_3$ | 2% $Cr_2O_3$ | |
| Calcium formate | 2.70 | 4.36 | 3.53 |
| Sodium bicarbonate | 2.70 | 4.40 | 3.55 |
| Sodium sulphite | 2.59 | 4.12 | 3.35 |
| Neutral syntan | 2.65 | 4.23 | 3.44 |
| Polymeric phosphate | 2.62 | 4.36 | 3.49 |
| Mean | 2.65 | 4.29 | 3.47 |

Calcium formate and sodium bicarbonate have had no influence on the chrome content, but sodium sulphite and to a lesser extent both the neutral syntan and the polymeric phosphate have reduced the chrome. This effect is more pronounced in those leathers which were tanned with the high level of chromium.

pH of Exhaust Tan Liquors

The pH of the residual tan liquor was measured at the end of tanning and these values are given below.

| | Level of Chrome Tannage | | Mean |
|---|---|---|---|
| | 1% $Cr_2O_3$ | 2% $Cr_2O_3$ | |
| Wattle | 4.5 | 4.1 | 4.3 |
| Quebracho (sulphited) | 4.3 | 4.0 | 4.1 |
| Chestnut (sweetened) | 3.5 | 3.4 | 3.4 |
| Wattle (sulphited) | 3.7 | 3.2 | 3.4 |
| Myrtan | 3.3 | 3.0 | 3.1 |
| No retannage | 3.5 | 3.3 | 3.4 |
| Mean | 3.8 | 3.5 | 3.6 |

The wattle and quebracho liquors had the highest pH values, the acidity being only slightly greater than in the original, the pH values of which were 4.6 and 4.4 respectively. There is a marked difference between the residual liquors from the low and high levels of chrome tannage, more acid being present in the latter case. Chestnut and the sulphited wattle both resulted in moderately acid liquors at the end of tannage, and myrtan liquors were very acid.

The type of neutralisation was also responsible for variations in pH, the alkalis tending to be better neutralising agents than the complex-forming materials.

| | Level of Chrome Tannage | | Mean |
|---|---|---|---|
| | 1% $Cr_2O_3$ | 2% $Cr_2O_3$ | |
| Calcium formate | 3.8 | 3.7 | 3.7 |
| Sodium bicarbonate | 4.0 | 3.8 | 3.9 |
| Sodium sulphite | 3.6 | 3.3 | 3.4 |
| Neutral syntan | 3.5 | 3.2 | 3.3 |
| Polymeric phosphate | 3.7 | 3.4 | 3.6 |
| Mean | 3.8 | 3.5 | 3.6 |

These figures show that calcium formate and sodium bicarbonate give the highest pH values whereas the neutral syntan and sodium sulphite treated leathers were still relatively acid. The leathers which had been neutralised with polymeric phosphate had intermediate pH values.

## DISCUSSION AND CONCLUSIONS

Many differences in the properties of leather can be attributed to the nature of the retanning material. Thus it is established by reference to the literature that factors such as plumpness, grain crack, break, tearing strength and shrinkage temperature will be affected by the choice of extract for retanning. Moreover, the type of leather required and the degree of retannage will determine the choice of extracts. Several independent workers have shown that either wattle or quebracho are particularly suitable in-so-far as these properties are concerned.

However, affinity factors have been neglected in many of the recently published reports in this field, and the work presented in this paper surveys some of the factors which are important. The level of chrome tannage is known markedly to influence the reactivity of chrome tanned hide substance and this is confirmed by the results given above. Of greater significance was the effect of the type of vegetable tanning extract used for retanning. Thus, in terms of weight increase, chestnut was shown to be the most effective although by suitable choice of conditions wattle and quebracho can be equally effective. On the other hand sulphited wattle had very much lower affinity. The effect of sulphiting is of considerable interest. Sulphiting increases solubility and this is probably achieved by breaking down loose aggregates (reducing particle size) as well as

It is evident that, of the vegetable tanning extracts studied, wattle and quebracho are the most effective for producing the properties needed in a retannage, namely, strong, plump leather with an elastic grain, but care must be exercised in the use of sulphited extracts since the sulphonic groups are likely to impart greater reactivity with the chromium yet reduce the affinity of the extract for the pelt. Sulphitation of wattle extract is not recommended if it is to be used for retanning.

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