

Bulletin of The Central Leather Research Institute

Vol. III

JUNE, 1957

No. 11

	CONTENTS	Page
Editorial Board: Dr. Y. NAYUDAMMA <i>(Editor)</i> Dr. S. K. BARAT Dr. S. N. SEN Mr. M. A. GHANI Mr. N. SUBRAMANIAN <i>(Secretary)</i>	Combination Tannages : Part IV—Combination Chrome Vegetable Tanning in Single Bath — <i>T. S. Ranganathan & Y. Nayudamma</i>	409
	Research Bears Fruit—Practical Demonstration No. 3—Process No. 2—Manufacture of Picking Band Leather by the Sulphur—Chrome Combination Tanning Method — <i>N. S. Bose</i>	419
	Research Bears Fruit—Practical Demonstration No. 5—The Manufacture of Glace Kid Leather by one bath Chrome Tanning—Process No. 1 — <i>J. C. Deb</i>	423
	Technical Seminar — Use of Dhawa Leaves for E. I. Tanning — <i>J. B. Rao</i>	429
	Classified Abstracts	430
	Patents	438
	Notes & News	440
	C. L. R. I. News	444
	Visitors	444

Annual Subscription.—Rs. 9/- (inland); Rs. 18/- (foreign); Single Copy As. 12.

The Bulletin of the Central Leather Research Institute is issued monthly.

Communications regarding contributions for publication in the Bulletin, books for review, subscriptions and advertisements should be made to the Secretary of the Editorial Board, C. L. R. I., Madras-20.

All remittances by cheque or money order should be made payable to the Director, Central Leather Research Institute.

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Bulletin of
The Central Leather
Research Institute
Madras



VOL. III

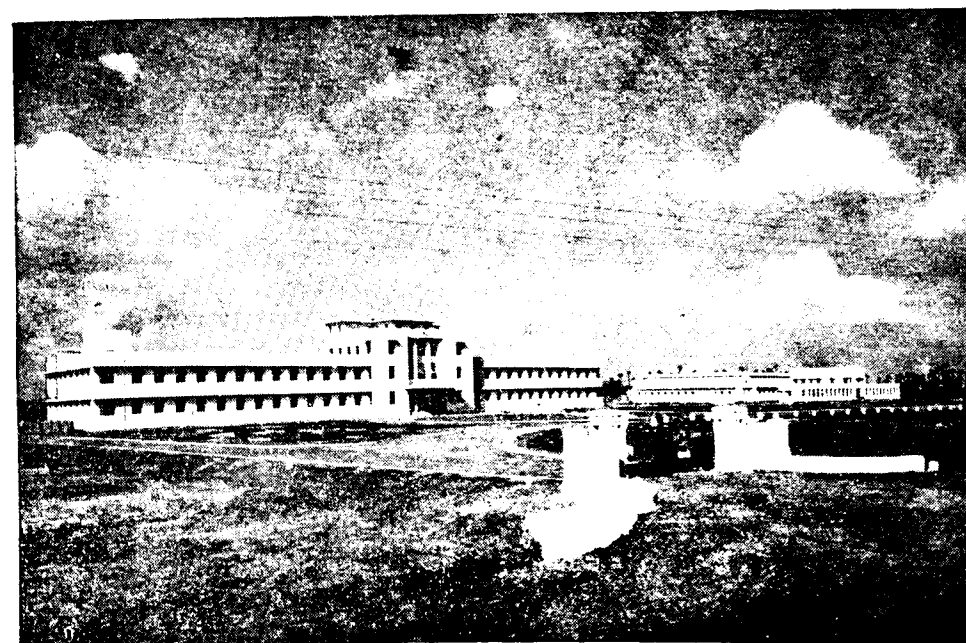
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**CENTRAL LEATHER RESEARCH INSTITUTE,
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COMBINATION TANNAGES: PART IV

Combination Chrome Vegetable Tanning in Single Bath *

T. S. RANGANATHAN & Y. NAYUDAMMA

SUMMARY

The advantage of a single bath combination tannage has been discussed and different methods of preparation of tan liquor containing both vegetable tannin and chrome had been dealt with with special reference to the reduction of dichromate by vegetable tannin in presence of acid. In the present study, method of preparation using divi-divi, owing to its easy availability and high sugar content, had been described. The characteristics of the liquors using varying amounts of vegetable tannin regarding its pH, acidity and basicity and the nature of the complex had been discussed. Ion exchange studies and potentiometric studies had been carried to find out the change in the nature of complex and buffering characteristics of liquors when increasing amount of tanning material is used for reduction. The probable nature of binding of the vegetable tannins and its degradation products to the chrome complex had been discussed from the data obtained.

320

The different tanning materials like chrome, vegetable tannin fish oil etc., produce different kinds of leathers, each with its own characteristic properties which are suitable for different purposes. For certain purposes, a leather may be required which has got the desirable properties of two or more of the known tanning agents. It is possible to impart the good qualities of different kinds of tanning to the same leather by pretanning the pelt with one kind of tanning material and retanning the same with a different tanning material, i.e. by combination tannage. This kind of mixed tannage not only influences the properties of the final leather but also sometimes reduces the time of tanning.

Of all combination tannages, the most widely used one is chrome vegetable combination tannage. The chrome tannage can precede the vegetable tannage, follow it or be applied with it. The first one is known as chrome retannage and the second semi-chrome tannage. Simultaneous vegetable and chrome had been little used, though mixed extracts were marketed. Combination chrome vegetable tanned leather is superior to chrome in fed and softness and to vegetable tanned leather in the speed of manufacture, strength, elasticity, durability and heat stability.

In the chrome retanning and semi chroming processes, two separate baths are required to effect the tannages one after the

* Forms part of thesis for M.Sc. degree of Madras University.

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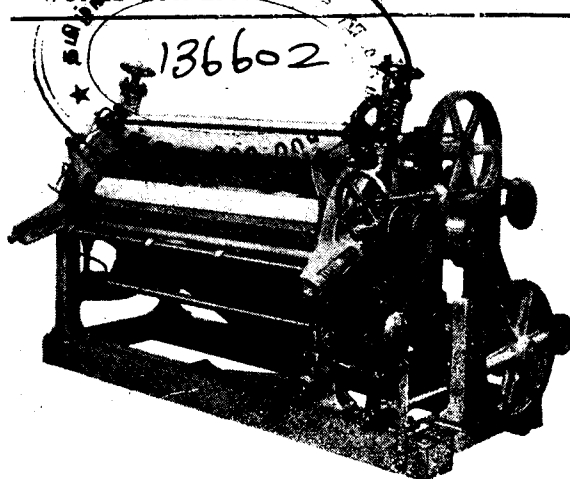
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Assistant Director-in-charge

**CENTRAL LEATHER RESEARCH INSTITUTE
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other. This means a long duration of time, more labour, power and to some extent wastage of tanning materials and chemicals. If both the tannages are carried out simultaneously, the above mentioned difficulties can be avoided. For this, it is necessary to prepare an extract or liquor which contains both basic chrome salts and the vegetable tannin, having the basic properties of a new tanning material obtained as a result of the inter-action of the two. This third material will be of advantage in imparting some special properties to the leathers. In the past, numerous efforts had been made to give a combination chrome vegetable tanning in single bath. A mixture of chrome alum and vegetable tannin was recommended (I) to produce a leather with predominating properties of vegetable tan. Woodroffe² reported that he was not successful with mixed extracts.

The extracts or liquors as suggested above may be made¹ by simple mixing of basic chrome liquors with vegetable tanliquors and² reducing the hexavalent chrome to trivalent form by an excess of vegetable tanning materials.

When mixing the two agents, i.e. chrome and vegetable liquors, precipitation is found to occur, if the conditions such as concentration, pH etc., are not properly controlled. The precipitation can be avoided only in very low concentrations. It might be, however, possible to prepare a combination chrome vegetable liquor by adding suitable stabilising agents, avoiding precipitation. Very recently it has been found possible to prepare such a liquor.³

Yet another method of preparing such an extract would be by reducing bichromate with excess vegetable tanning material in presence of acid. This process is more or less similar to preparing chrome liquors from bichromate by reduction with organic materials like sugar, molasses, glycerine, sawdust etc. When bichromate is reduced with just the sufficient amount of a vegetable tanning material, the liquor will have properties similar to the liquors reduced with sugar, molasses or sawdust. When more of the vegetable tanning material is used, the liquors should have better properties, because of the presence of still greater amounts of organic materials and should produce plumper and fuller leathers. Also there should be free vegetable tanning material which will have its own tanning effect. So much so, by such a liquor, one could produce the effect of both the chrome salts and vegetable tanning material.

The reduction of bichromate with the tanning material may be done by adding the sulphuric acid to the mixture of bichromate and the vegetable tanning material. Previous studies^{3a} indicated that, of different systems of reduction the addition of acid to bichromate tanning material mixture, was better in the way of producing the tanliquor having the characteristics of both chrome and vegetable tannin.

Any vegetable tanning material can be used for reduction. The tanliquor produced from different types of vegetable tanning agents may give different tanning characteristics. In this present work, divi-divi has been used for the production of mixed tanning liquors. This has been chosen because it is available in plenty in India and this is not used to a great extent as such in vegetable tanning, since the leach liquor from it readily ferments. In addition, this material contains not only organic tanning substances but also a good amount of valuable sugars which will give a better chrome liquor.

*Preparation of liquors*⁴: The organic matter content of the material was determined and the amount that was just sufficient to reduce a fixed amount of bichromate was first determined. The tanliquors were prepared by reducing a mixture of 100 gms. of bichromate and 84 gms. of conc. sulphuric acid (1.84 sp. gr.) with differing amounts of the divi-divi powder. These are given in the table :

Liquor No.	Organic matter content of the Divi-divi powder, used : 86.8%			pH of the resulting tanliquor
	Bichromate	% Divi-divi	% Acid	
1	150 gms.	40	84	2.850
2	"	45	"	2.850
3	"	50	"	2.850
4	"	55	"	2.775
5	"	60	"	2.750
6	"	65	"	2.625
7	"	70	"	2.550
8	"	80	"	2.450
9	"	90	"	2.450
10	"	100	"	2.400

The sodiumbichromate was dissolved in about 400 cc. of water and the powdered tanning material was added and stirred when the requisite amount of sulphuric acid was slowly added with constant stirring. The reduction was carried out on a boil-

ing water bath to maintain uniformity in the temperature of reduction. The reduction was complete in two hours. The liquors were cooled and allowed to age for about 15 days and then filtered through cloth collected and stored in well stoppered bottles.

The liquors could be used as such for tanning purposes in the same way as a basic chrome liquor is used in tanning. The liquors could be also concentrated and made into powder form by spray drying. For use the powders have to be simply dissolved in slightly hot or warm water. The colours of the liquors tended towards brown to dark brown with increasing amounts of vegetable tanning material in the liquor.

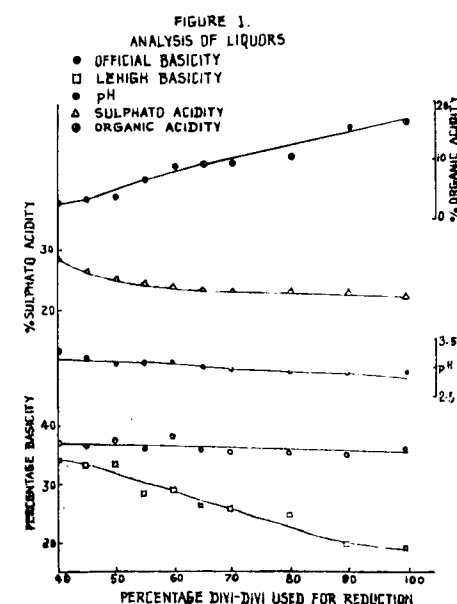
Liquor analysis: The tanliquors prepared as above were analysed for (a) chrome content by the method of Cameron and Adams^{4a} using perchloric acid, (b) basicity and acidity by Procter McCandlish titration⁵ as well as by the Lehigh method⁶, (c) pH, and (d) complexly held acid radicals. The results are given in Table I and Figure 1.

TABLE I

No.	Divi-divi used for 100 gm. Bich.	Basicity		Comp. held org. aci- dity	% Sulphate Acidity (Comp.)	% Cr ₂ O ₃	pH of Anal. SOL
		Official	Lehigh				
1	40	37.12	34.06	3.14	28.78	7.66	3.3
2	45	36.77	33.20	3.57	26.62	5.37	3.2
3	50	37.53	33.32	4.23	25.30	5.60	3.1
4	55	36.09	28.42	7.07	24.51	5.63	3.1
5	60	38.13	28.77	9.36	24.35	7.83	3.1
6	65	36.02	26.45	9.57	23.46	5.75	3.05
7	70	35.72	25.89	9.82	23.19	5.56	2.975
8	80	35.46	24.90	10.56	22.93	4.96	2.95
9	90	35.18	20.01	15.17	22.63	5.05	2.9
10	100	35.56	19.37	16.19	21.77	5.61	2.9

Divi-divi as such contains acids, salts, and sugar apart from tannins and non-tannins. During the course of reduction of bichromate, this complex material breaks up further yielding more acids and other broken down molecules of varying sizes. Some or all of these constituents may have the power of penetrating the chrome complex. Evidence is available⁷ for the penetration of tans and non-tans apart from organic acids and therefore it is quite probable that such penetration occurs in this case also. This is confirmed by the decreasing sulphate content of the

chrome complex in the liquors prepared. The possibility of tannins and similar compounds being attached directly to chrome



replacing aquo groups and also some of the SO₄ groups favouring the formation of neutral and anionic chrome complexes had been suggested.^{8,9}

Vegetable tannins of the pyrogallol type contain a varying percentage of weak organic acids of the gallic acid type which would form stable complexes with basic chrome sulphate. Pyrogallol tannins also contain hydroxy groups which behave as weak acids. It has been suggested⁹ that the formation of a ring structure with the chromium is essential to provide a stable complex and that the tannins containing organic acid groups form the most stable complexes. From these it is clear that the vegetable tanning material and its degradation products do form complexes with chrome salts. The results obtained confirm the possibilities suggested that the addition of tannin to a basic chrome sulphate will cause a decrease in the positively complexes which lose their charge and become neutral⁷ and that the acidity will increase while the sulphate content of complex decreases. These changes can be explained only by the entering of the vegetable tanning material or its degraded molecules into the cationic chrome complex. Tanning material replaces the sulphate groups as a constituent bound by the main valencies. At the same time a certain part of the tanning material enters into the chrome complex as a

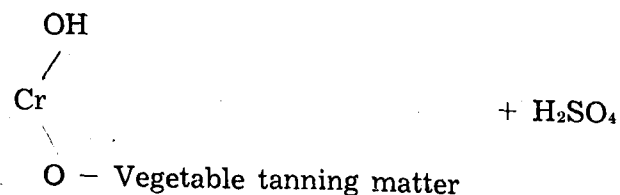
co-ordinately bound constituent, probably replacing the neutral water molecules, thereby decreasing the net charge of the complex.

From the overall (Lehigh) basicity, it is seen that the acidity increases when the amount of divi-divi used is increased. The official basicity by the Procter McCandlish titration is obtained indirectly by deducting the sulphate acidity from 100. This method yields erroneous results in certain cases,^{10, 2, 12} as some of the organic acids are not replaced by hydroxide but remain in the complex.

Examining the data above, if the organic acids penetrate the complex, SO_4 in the complex will be reduced and therefore the official basicity should increase. But remained the same. This may show that whatever organic acids or degradation products that have replaced the SO_4 have a power greater than that of SO_4 but lower than that of the (OH) . Therefore in the Procter McCandlish titration, these are displaced to give the same original basicity value.

If OH also is removed partly by the vegetable material or its degraded molecules permanently (even then the official basicity which depends upon the acid groups only will not affect the value), the basicity by the Lehigh method, however, should show the correct picture of the complex, since it measures only the OH groups in the complex. That the overall basicity is decreased means that the OH groups have also been displaced. It seems as though the vegetable tanning material (or its degraded molecules) is not only displacing water and SO_4 but also a part of the OH groups, but this replacement of OH is not by a very strong bond like the oxalate ion but a weak one, but stronger than hydrogen bond or neutral water molecules or sulphate radicals.

The probable bonding may be as follows, the OH of the complex and the OH or other similar reactive groups of the vegetable tanning material combining, eliminating water, ($\text{Cr}-\text{O}$ Vegetable tanning matter). Yet another possibility of the reaction is the vegetable matter reacting through its hydroxy groups displacing SO_4 resulting in acid



The decrease in pH also shows that the SO_4 groups are displaced by the vegetable tanning material producing sulphuric acid. Since the pH decrease is only about 0.4 units, it is likely that no strong acids like oxalic acid are involved. On the other hand, it may be a good buffering system, requiring a greater amount of acid to show a marked change in pH. The degraded molecules of the vegetable tanning material may contribute to this good buffer system.

Ion-exchange studies :

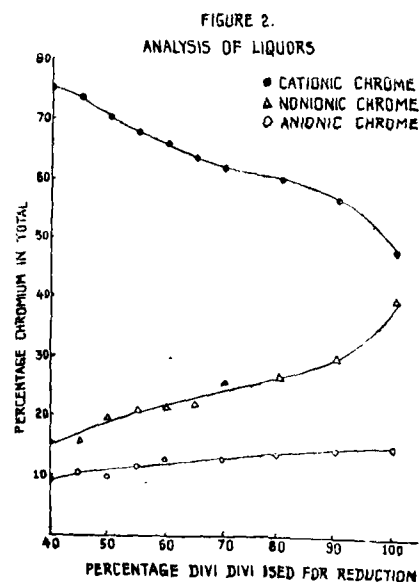
The different ionic i.e., cationic, anionic, and nonionic chrome contents of these liquors were then determined¹³ using Amberlite IR 120 analytical grade and Amberlite IRA 400 analytical grade. The results thus obtained are given in Table II and Fig. 2.

TABLE II

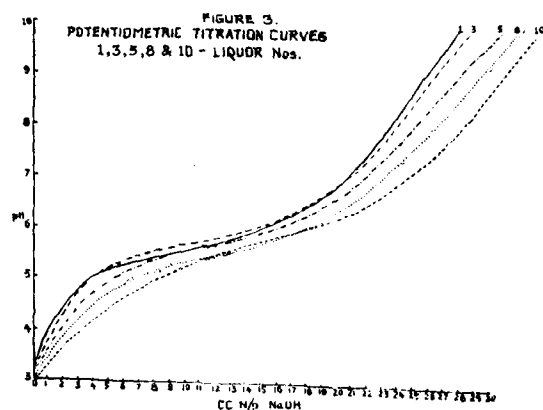
No.	Divi-divi used for 100 gm. bichromate	% cationic Cr	% Anionic Cr	% Nonionic Cr
1	40	75.08	9.29	15.63
2	45	73.62	10.58	15.80
3	50	70.25	10.01	19.74
4	55	67.74	11.40	20.86
5	60	65.92	12.73	21.35
6	65	63.34	14.95	21.71
7	70	61.69	12.94	25.37
8	80	59.94	13.59	26.47
9	90	56.10	14.19	29.71
10	100	47.50	14.53	37.97

The fact that there is more nonionic chrome when more divi-divi is used, confirms the postulate stated earlier that more and more vegetable matter penetrates into the chrome complex to make it less cationic — at the same time the affinity is not so great as oxalate to make it anionic. It is therefore probable, the first transformation is to nonionic before it goes into anionic stage. Vegetable tannin may displace SO_4 or OH ions or the neutral water molecules. The charge will be reduced if the neutral water molecules are displaced by the anions of the vegetable molecules. Such is the case as confirmed by the fact that there is an increase in the nonionic content with increase in the amount of divi-divi used in reduction. It is also possible that the nonionic complex may be further converted into anionic particularly if the complexing ions have greater affinity to chrome, e.g. oxalate ion readily penetrates basic chrome complex, and

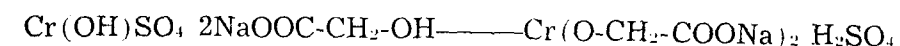
forms an anionic complex. The fact that the anionic complex has not been much increased may indicate that the vegetable molecule is not so powerful a complexing agent.



Potentiometric studies: In order to find out further the nature and constitution of veg-chrome liquors prepared, potentiometric titrations of these liquors were carried out. An amount of the liquor containing 0.5 gm. Cr_2O_3 was pipetted out into a beaker and the total volume was brought to 100 cc. by the addition of carbondioxide free distilled water. This was then titrated with N/2 carbonate free sodium hydroxide, the pH being noted after the addition of 1cc. of the alkali and stirring for a minute. Then the curve was drawn with pH against cc. of alkali.



It is observed from the curves that there is a certain amount of buffering action due to the increase in the amount of the vegetable tannin in these liquors. Moreover it is observed that the curves shift towards the right as the divi-divi content is increased. Studying the effect of different masking salts in chrome liquors, Thorstensen and Theis¹⁴ observed that hydroxy acids like glycolate behaved differently as compared to other carboxylic acids. In comparison with an unmasked chrome liquors, the titration curves were displaced to the right in the case of the addition of glycolate rather than to the left as was the case with other masking agents such as formate, acetate etc., i.e. more NaOH was needed in the titration to arrive at the same pH. It was suggested that co-ordination had taken place through the hydroxy groups of the glycolate as shown below.



In the veg-chrome liquors also, the curves are shifted to the right. It is, therefore, probable that the organic matter of the divi-divi powder might co-ordinate similarly with the chrome complex as indicated above i.e. $\text{Cr}(\text{OH})\text{SO}_4$ Vegetable matter $\longrightarrow \text{Cr} \begin{smallmatrix} \text{OH} \\ \text{O} \end{smallmatrix}$ Veg. matter H_2SO_4 . These curves seem to confirm the possibility suggested previously that the vegetable organic matter displaced SO_4 and the OH in the manner stated. From these it is seen that the vegetable matter or its degradation products can attach itself to OH of the chrome complex, producing water, accounting for a decrease in the Lehigh basicity, or can attach itself directly to chromium displacing SO_4 and producing sulphuric acid causing a shift to the right of the potentiometric titration curves. Since both have been observed, it can be concluded that a part of the vegetable tanning matter attaches to chrome through-OH and a part of the type of glycolate attaches to chrome directly.

In the light of the results and discussions made, it can be seen that these veg-chrome liquors are essentially chrome liquors and more or less similar to chrome liquors made using sugar, molasses, sawdust or glycerine, differing only in the amounts and nature of the organic acids produced in the reduction and the presence of some organic degradation products of tannin of varying sizes which gave special characteristics to the leathers tanned with them which will be discussed in a later paper. Some neutral molecules from the vegetable tanning material may also displace the neutral water molecules in the complex.

Chem. & Physics Division,
Dated 29th April, 1957.

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RESEARCH BEARS FRUIT

Practical Demonstration No. 3

Process No. 2: Manufacture of picking band leather by the Sulphur-Chrome combination tanning method *

S. N. BOSE

Raw material : The raw materials are slaughtered or green prime quality heavy buff. or ox hide weighing 85 lbs. and up or wet salted prime buff. or ox hide weighing 75 to 80 lbs. The hides should be free from flay cuts, warble holes etc. The raw weight is recorded and all the percentages mentioned below are based on this weight.

Soaking : The slaughtered or green hides are soaked overnight in 500% water containing $\frac{1}{4}$ % caustic soda, 7% common salt and $\frac{3}{4}$ lb of bleaching powder per 500 lbs of water.

The soaked hides are washed in two to three changes of water and then rounded into butt, belly and shoulder. The butt portions are fleshed, washed and horsed up for $\frac{1}{2}$ hour. The belly and shoulder pieces may be processed into either picker, lace or sole leathers.

Liming : The butts are painted on both sides with the following paste and kept in pile overnight in the bottom of a pit.

Sodium sulphide (fused)	2%
Slaked lime	5%
Water	15%

If there be any paint left, it may be spread over the butts in the pit.

Next day the painted butts are taken out and a lime liquor is prepared with 5% slaked lime and 250% water. They are handled in this liquor for 10 minutes and left for 2 hours. Then the butts are hauled up and replaced twice, once in the afternoon and again in the evening and then they are kept well immersed in the liquor overnight after adding 3% salt.

* Process demonstrated to farmers during 5th April to 14th May, 1957.

Next day, the limed butts are trampled for 30 minutes in $\frac{1}{2}\%$ sodium Bicarbonate and 300% water. Then they are washed in plain water, unhaired and then fleshed. The goods are weighed and washed again in two changes of water in the drum. Percentages mentioned below are based on the pelt weight.

Deliming :

The butts are delimed using 3% Ammonium sulphate and 150% water.

The drum containing the butts in this solution is run for one hour (speed of the drum 10 r.p.m.) stopped for one hour, again run for one hour and then the butts are left in the bath overnight. Next day, the drum is run for one hour and a cut section is tested with phenolphthalein. If it shows natural colour, it indicates that the hides have been delimed. If this is satisfactory, the delimed pelts are scudded, washed in 2 changes of plain water and pickled.

<i>Pickling :</i> Sulphuric acid (66 Be)	2% on pelt weight
Common salt	10% „
Water	100% „

7% common salt is dissolved in 100% water in the drum and then 1% acid is added to it and drum run for 10 minutes after which the goods are put in and the drum is run for one hour and kept at rest for the following one hour. In the meantime about 10% of the pickle liquor from the drum is taken out and the remaining quantity of salt i.e. 3% salt is dissolved in 8% of this pickle solution and 1% acid is diluted with 2% pickle solution and kept for one hour. The drum is run and acid and salt solutions are mixed together and added in a slow stream in 15 minutes and the drum is run for 45 minutes more and then stopped for 1 hour. After that, the drum is again run for 15 minutes and then the goods are kept well immersed in the liquor overnight. Next day, the drum is run for 1 hour and stopped for one hour and then again run for 15 minutes and stopped for 45 minutes. This may be continued till the evening over a period of 6 to 8 hours. A cut section is tested with Methyl red indicator and it should show pink colour right through the thickness.

Depickling : The goods are then depickled with 11% Hypo and 75% water.

Hypo solution is prepared in the drum next morning. Goods are put in and the drum is run for one hour and stopped for one

hour. This is repeated till the total drumming is done for four hours. Then the depickled goods are horsed up in the evening for overnight.

Chrome liquor preparation :

Bichromate of soda	10 parts
(98% purity)	
Sulphuric acid (66° Be)	11 parts
Molasses	2½ to 3 parts
Water	30 parts.

10 parts bichromate of soda are dissolved in 20 parts of water. 2½ to 3 parts of molasses are mixed with 10 parts of boiling water. The acid is added to the Bichromate solution and the Molasses solution is added in continuous small stream to the bichromate and acid mixture already taken in a Lead-lined vessel in about 30 minutes whereafter the whole mass turns into bluish green colour. This is stored for a week whereafter it may be used.

Procter basicity of this liquor will be approximately 108-110 The pH of the liquor will be approximately 2.0.

Chrome tanning : 3% common salt is dissolved in 100% water in a drum. The first instalment of chrome liquor is added to the drum and the goods are put in and drummed for 30 minutes whereafter the second instalment is added and drum run for one hour. The drum is run again after stopping for one hour and then the 3rd and last instalment is added. The drum is stopped for one hour again run for one hour, rest for one hour and then run for 2 hours and left the goods in the liquor overnight. Next day the drum is run for 1 to 2 hours when penetration will be over. Altogether 5% Bichromate equivalent chrome liquor is used in tanning. As soon as the penetration is over, take 1.25% sodium bicarb. is taken and dissolved it in 10 times its weight of warm water and then added the bicarb. solution in 3 instalments at an interval of ½ to ¾ hour. After last addition of bicarbonate solution, the drum is run for 3 hours and then left the goods overnight in the liquor. Next morning, the drum is run for one hour and horsed up the tanned goods for 1 to 2 days. A cut piece will stand boiling test for 3 minutes (R.P.M. of tanning drum is 8 to 10). (All the percentages are calculated on pelt weight).

Sammying, splitting and shaving : The tanned goods are sammed, splitted and shaved to about 6 mm. Shaved weight is noted.

Washing, neutralisation and fatliquoring :

The shaved leathers are washed in 2 changes of water and then neutralised with 4% Hypo and 200% water for 2 hours. The neutralised leathers are again washed in 2 changes of water and may be dyed with $\frac{1}{4}$ % of any suitable shade acid or direct dye and 100% water at 50°C for 30 minutes and then they may be fatliquored in the following bath for 45 minutes.

Turkey Red Oil	2%	on shaved weight.
Neatsfoot oil	$\frac{1}{4}$ %	„
Soft soap	$\frac{3}{4}$ %	„
Water at 60°C	100%	„
Paranitrophenol	1%	on the weight of the mixture of T.R.O. Neatsfoot oil and Soft soap.

The fatliquored leathers are horsed up for one day, then they are sammed and stuffed as follows :

Stuffing :

Mutton tallow	13 $\frac{1}{3}$ %	on sammed weight.
Fish oil	62 $\frac{2}{3}$ %	„
Stearine	1 $\frac{1}{4}$ %	„
Paraffin wax	1 $\frac{1}{4}$ %	„

Stearine, paraffin wax, tallow are melted and fish oil is added to it and temperature of the whole mixture is raised to 70°C. In the meantime, the stuffing drum is heated to about 70°C. by passing hot air, the melted stuffing material is fed in, goods are introduced and the drum is run for one hour whereafter they may be hung up in a hot room of temperature 50°C. for a week in order to distribute the fats more uniformly. Then they may be set and stretched for one day. Then they may be taken out and cut into straps. 1% of "oildag" i.e. oil dispersible graphite may be used along with the other ingredients in order to make the leather fibres to be more heat-resistant and abrasion resistant and also to minimise the stretch of the leathers.

RESEARCH BEARS FRUIT

Practical Demonstration No. 5

The manufacture of glace kid leather by one bath chrome tanning.

Process No. 1 *

J. C. DEB

Raw Material : Wet salted Erode quality goat skins are taken, size being 30"-34".

Soaking : The skins are soaked for two hours in plain water to remove the salt. They are then taken out, trimmed, broken over the beam and washed thoroughly in running water for one hour. The skins are taken out, drained and weighed for liming.

Liming : (By paste method) : The unhairing is done by pasting a depilating paste of the following composition.

Sodium sulphide	1 part	: 4 lbs per 100 skins
Sodium chloride	5 parts	: 20 lbs „
Slaked lime	15 parts	: 60 lbs „

Sodium sulphide and common salt are dissolved separately in water. The two solutions are then added to the mixture of lime and water. Care is taken to get a homogeneous paste and cooled to room temperature. It is better to prepare the paste two days earlier before the application on the skins.

The paste is applied to the flesh side of the skins. The skins are then piled up on a platform flesh to flesh for two days. On the 3rd day, the skins are unhaired and put into new lime liquor containing 5% lime on the soaked weight in a paddle for 4 days. The paddle is run for 30 minutes in the morning and 30 minutes in the evening everyday during these four days. On the 6th day, the skins are taken out, fleshed, scudded, weighed and washed thoroughly in running water at 90°F for 20 minutes in a paddle. The skins are then removed from the paddle and are ready for bating.

Bating : (Overnight bating method is followed).

The washed skins are bated in a covered paddle, using 1.0% Pancreol 5A on the fleshed weight. The bath is made with half

* Process demonstrated during June, 1957.

the quantity of bate using 300% water at 95°F and the skins are run for one hour. After running for one hour, 2 oz. potassium or sodium fluoride dissolved in one pint of water at 105°F is added to the bath and the bath of 100 gallons liquor, is run for 5 minutes. The skins are left in the bath overnight, keeping down the temperature of the bath at 90°F.

Next morning, the remaining half of the bate is added and the temperature of the bath is raised to 100°F by passing steam. The skins are paddled in the bath controlling the temperature of the bath at 100°F until satisfactorily bated. The pH of the bate liquor before unloading should be 7.8 to 8.0 if not it should be adjusted to that pH.

The exact stage when the bating can be regarded to have been satisfactorily completed is judged by the following indications: (i) The skin should be thoroughly delimed and phenolphthalein applied to the edge of a cut piece of bated pelt not show a red colouration. (ii) The bated skins should be absolutely fallen and flaccid and should lie in any position in which it is kept. They should not show any tendency to spring back. This can be tested by pressing the grain of the skin by the thumb and thumb impression should remain. (iii) When the bated skins are scratched on the grain by the thumb nail, the scud consisting broken hair roots, either epidermal remnants, dirt etc. should easily come out showing that the scud has been thoroughly loosened and rendered easily removable. (iv) When air is enclosed by folding the bated skin in the form of a pouch and the pouch is squeezed by the hand and made smaller and smaller in volume, then all the enclosed air should come out produced air bubbles on the surface of the pouch. This shows that the pores of the skin have been thoroughly opened out. (v) When the flesh side is scratched by the thumb nail, the adhering flesh should be removable when some pressure is applied, but the flesh should not be too easily removable, as in the case of over bating.

The skins are then taken out, scudded well, washed in cold water of 90°F and then put into the pickling process.

Pickling: The skins are pickled overnight in a drum using the following composition.

	% on the fleshed weight.
Common salt	12
Sulphuric acid	1½
Water	100

424

Salt is first dissolved in water and the skins are put in the drum and run for 5 minutes. The sulphuric acid is then diluted and added to the revolving drum through the hollow axle and the skins are run one hour and left the skins in the pickle bath overnight.

Next morning the skins are drummed for 30 minutes to one hour and the pH is adjusted to 1.8 to 2. After pickling, the pickle liquor is run off but the pickled skins are allowed to remain in the drum so that the pickle liquor is not drained off the skins.

Tanning: Tanning is done in the pickle drum in which the pickled skins are already there. One bath process is followed. The chrome liquor is made from bichromate of soda, sulphuric acid, molasses. The basicity of the prepared liquor is 96 (Proctor).

Preparation of chrome liquor:

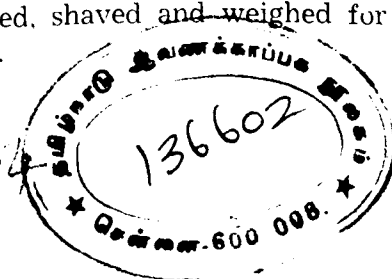
Bichromate of soda	100 lbs.
Sulphuric acid	90 lbs.
Molasses	40 lbs.
Water to make	50 gallons.

At first a small quantity of water, about 2½ glns. for a park of 100 lbs. skins is added. This water together with the water in the pickled skins is sufficient. To this, chrome liquor diluted with 50% water on the fleshed weight of the skin is added in 3 instalments. First instalment is added through the hollow axle into the running drum and drummed for 30 minutes. Then added the second instalment and run for one hour. Then added last instalment and run for 3 hours more and left overnight. Total quantity of liquor used is equivalent to 5% bichromate of soda on the fleshed weight.

Next morning, the drum is run for 30 minutes and 10% Hypo on the fleshed weight is dissolved in small quantity of water is added to the running drum in two instalments at an interval of 30 minutes. The drum is run for two hours more. The pH of the skin should be 3.6 to 3.8. When the boiling test is satisfied, tanning is completed. The skins are then washed in diluting the chrome bath for 10 to 15 minutes and piled up on the platform for 2 to 4 days to drain of the excess of moisture.

Sammying and Shaving: The skins are then slicked or putting out on the flesh side, sammed, shaved and weighed for neutralising, dyeing and fatliquoring.

51
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Neutralising: The skins after thorough washing are neutralised for 30 minutes with the sodium bicarbonate solution containing sodium bicarbonate 1% and water 200% (percentage on the shaved weight). The skins are put into the solution, drummed continuously for 30 minutes and tested for proper neutralisation with bromo cresol purple. A purple colour on the leather surface and yellow colour in the middle layer indicate proper neutralisation. The pH of the skin is checked to 5.6.

Washing, dyeing and fatliquoring: The skins are washed for 10 minutes at 130°F in a wooden vat and ready for dyeing. For blacks the skins are dyed with the following.

	% on the shaved weight.
Chlorozal black	1
Nigrosine	1½
Methylene Black	½
Formic acid	½
Water	200 at 130°F.

The skins are put turned over (grain side out) into the drum containing 200% water at 130°F. Chlorozal black dissolved in water is added in the drum. Start the drum and run for 15 mts. Then added the nigrosine, dissolved separately and run the skins for 15 mts. more. The methic black is also dissolved separately and added to the drum and run for further 15 mts. Lastly added the formic acid and run the drum for 10 mts. more.

The skins are then fatliquored in the same bath with the following composition on the shaved weight of the skins for 45 mts. at 130°F.

Neatsfoot oil	1¼% on the shaved wt.
Egg oil (or egg yolk)	½% „
Cremol F	½% „
Soap solution (10% solution)	4 oz.

pH of the emulsion fatliquor adjusted to 7.8 to 8. Then 2% Quebracho extract dissolved separately is added to the exhaust fatliquor bath and run for 30 minutes. The skins are then taken out and horsed up overnight.

Striking out and oiling up:

Next day, the skins are struck out on the flesh and grain side. Then neatsfoot oil is applied on the grain side and hung up in the shed for sammying.

Sammying, setting and drying: After oiling up, the skins are sammed, set out and dried in the shed.

Finishing:

(a) *Sawdusting, staking and buffing:*—The dry skins are stored for some days for conditioning. Then they are sawdusted overnight in moist sawdust to condition them for staking. The conditioned skins are staked first lightly by a slocomb staking machine. Then they are piled up on the floor in several packs contained one dozen skins in a pack for overnight. Next morning, the skins are staked again by the same machine with considerable pressure. They are then aired a little and buffed on the flesh side by the buffing machine using No. 120 grit emery paper.

(b) *Trimming and ironing:* Next morning, the buffed skins are trimmed and ironed on the grain side by a hand electric iron. The skins are now ready for seasoning.

(c) *Seasoning and glazing:* The skins are then given two successive coats of bottom season on the grain with the following:

Bottom season:

C.L.R.I. black pigment	8 oz.
Nigrosine	1 oz.
C.L.R.I. M.G. binder	4 oz.
C.L.R.I. glazing Finish No. 1	8 oz.
Ox blood	20 oz.
Milk	16 oz.
Green dye	3 gms.
Isopropyl alcohol	2 oz.
Diethylene glycol	½ oz.
T.R.O.	½ oz.
Ammonia	1 oz.
Water to make one gallon.	

After application of two successive pad coats with the above, the skins are dried, glazed and then given a top season coat

Top season:	Bottom season	2½ lbs.
CLRI M.G. Binder No. 1		2 oz.
CLRI. glazing finish No. 1		8 oz.
Milk		12 oz.
Blood		8 oz.
Formaldehyde		6 oz.
		Water to make one gallon.

One coat of the above is applied to the grain side with a brush, dried, and then apply the fixing coat by spray with

10% casein solution	1 part
Formaldehyde	1 part
Water	6 parts

The skins are then dried and put to the final glazing.

Final Glazing: Inclined bed glazing machine is the best for this type of leather. First glazing is done under heavy pressure moving the skins alround. The glazing produces glass marks on the grain which are smoothed out by glazing under light pressure, the second time. The glazing is skilfully done without producing pleats.

Smooth plating, measuring, ironing, grading and packing:

The glazed skins are then measured and smooth plated by hydraulic press at 150°F with light pressure. The skins are then ironed with an electric iron if necessary and then sorted, graded according to substance into 3 or 4 classes. They are then packed with 24 skins in a bundle.

TECHNICAL SEMINAR

*Use of Dhawa leaves for E.I. tanning.**

J. B. RAO

The utilisation of Dhawa leaves in East India tannage has been studied. The material by itself has not been found to be useful as it imparts greenish tinge to the leathers tanned with the same. However, blend of the leaves with Goran and Karada which are by themselves unsuitable for E. I. tanning, have been found to yield leathers of good quality similar to those produced with imported wattle bark. Thus the individual defects of Dhawa, Karada and Goran are overcome by suitably blending them and the blends can be used in place of imported wattle bark in E.I. tannage.

* Summary of the Seminar held on 20th May 1957.

CLASSIFIED ABSTRACTS

RAW MATERIALS

DAMAGE TO PELT CAUSED BY OVERHEATING DURING DRYING. R. G. Mitton and C. D. Pomeroy. *J.S.L.T.C.* **41**, 3, 109, (1957). Skins cured by drying in tropical sunlight while in contact with the ground often show no signs of damage until put into lime, but then develop numerous holes. As it was suspected that this damage is associated with overheating of the skins while still damp, experimental pieces of skin were heated to various temperatures and for various times in the laboratory. These, too, showed little signs of damage until put into lime, when they disintegrated. The results indicate that damage is only likely if some parts of the skin reach the shrinkage temperature while still damp; if their maximum temperature is only a few degrees lower, little or no damage is likely, even if the heating is for some hours. A test for crackiness may be of value in deciding before processing whether skins have been heat damaged in drying.

SKIN STRUCTURE OF EGYPTIAN BUFFALOES AND CATTLE, WITH PARTICULAR REFERENCE TO SWEAT GLANDS. E. S. E. Hafez, A. L. Badreldin and M. S. Shafei, *J. Agric. Sci.* 1955, 46, 19; *Vet. Bull.*, 1956, 26, 349. *Via. J.S.L.T.C.* **41**, 1, 33, (1957). The skin of buffaloes is thicker than that of cattle; the number of hair follicles and of sweat glands per sq. cm. of skin is 394 as compared with 2,633 in cattle. There are twice as many sebaceous glands in buffaloes. Species differences in the distribution of blood vessels and capillaries and age differences in skin histology are described.

IMPROVED METHOD OF DISINFECTING SKINS CONTAMINATED WITH ANTHRAX. P. K. Boyarshinov. *Rep. 1st Soviet Conf. vet. Disinfect.*, 1951, 113; *vet. Bull.* 1956, 26, 181. Skins are soaked for at least 48 hr. in an aqueous solution containing 2.4% sodium bisulphite and 8% sodium chloride: the weight of solution is five times the dry weight of the skins. The skins are then transferred to an equal volume of solution of 5% hydrochloric acid and 12% sodium chloride for 30 hr. at 23°C for thin, and 30°C for thick, skins. The process is carried out in drums; the solution is previously deaerated.

PROCESSES PRIOR TO TANNING

FORMATION OF THIOSULFATE DURING LIMING OF CYSTINE. J. Pouradier and A. M. Venet. *Sci. et inds. phot.*, (2)27:297-300, August 1956. *Communication No. 1777V. Via. Mon. Abst. Bull.* **42**, 9, 512, (1956). Cystine was tested as a possible source of sulfur-sensitizers present in photographic gelatins. Ten grams of cystine were added to a suspension of 10 gm. of lime in 300 ml. of water. The mixture was kept at room temperature (19° to 22°C). Samples were removed from

time to time over the course of several months and, after removal of calcium by precipitation with ammonium oxalate, the samples were analysed by paper electrophoresis. Sulfide was present, as shown by the odor and by reaction with lead acetate. The electrophoresis showed the presence of at least four sulfur compounds: a weakly mobile cation, an uncharged compound, a moderately mobile anion, and a very mobile anion. The latter was identified as thiosulfate, present in small quantities and probably formed by aerial oxidation of sulfide.

TANNING

VEGETABLE TANNING

THE VEGETABLE TANNAGE OF SHEEPSKINS: A SYSTEMATIC STUDY OF THE INFLUENCE OF VARIOUS FACTORS IN THE TANNING. PROCESS-I. By M. F. Chambers, M. Dempsey, R. G. Mitton and E. F. Natrass. *J.S.L.T.C.* **41**, 1, 7, (1957). Sheepskins were vegetable tanned after bating and after eight weeks in pickle, using tanliquors of pH 2, 3, 4 and 5 and with salt contents near 0, 2, 4 and 6%. The tans used were mimosa and chestnut, in amounts of 10.8% and 16.2% (actual tan) on the bated weight, and the skins were dried to crust and subsequently given firm and soft finishes. Details are given of the tannages, and the analyses and tests made are enumerated. The results of these will be described in later papers.

THE VEGETABLE TANNAGE OF SHEEPSKINS: A SYSTEMATIC STUDY OF VARIOUS FACTORS IN THE TANNING PROCESS-II. By M. F. Chambers R. G. Mitton, and E. F. Natrass. *J.S.L.T.C.* **41**, 2, 48, (1957). Chemical analyses and manual assessments have been made on vegetable-tanned sheepskins, the treatment of which had been systematically varied (see part I). The extents to which the leathers darkened during exposure to light have also been assessed. The results of the analyses and assessments are described. Higher degrees of tannage were obtained with mimosa than with chestnut liquors, and by use of liquors with higher tan content. Degree of tannage varied in a complex manner with the acid and salt content of the tanliquors. The greatest fullness and firmness was obtained with liquors of low pH and low salt content, but at the expense of a greater tendency to drawn grain, particularly when the tan content of the liquors was high.

THE VEGETABLE TANNAGE OF SHEEPSKINS: A SYSTEMATIC STUDY OF THE INFLUENCE OF VARIOUS FACTORS IN THE TANNING PROCESS—III. THE PHYSICAL PROPERTIES OF THE LEATHERS. M. F. Chambers, R. G. Mitton and E. F. Natrass. *J.S.L.T.C.* **41**, 3, 94, (1957). An account is given of the results of physical and mechanical tests made on the sheepskin leathers whose tannages and chemical analyses were described in earlier papers^{1,2}. Although the acid and salt contents of the mimosa and chestnut tanliquors were adjusted to equality and both were used at similar concentrations, there are substantial differences in the properties of the leathers, the chestnut being appreciably firmer and stiffer, but thinner and of smaller area. The manner of finishing (firm or soft dressing) affected the properties materially, but the differences between skins stored in pickle and those

not pickled were relatively slight; such differences as existed showed that the pickled skins were thicker, less firm, and slightly weaker as judged by the tensile test. Major changes in properties resulted from variation of salt content and pH of tannage, particularly when both were low. These are summarised in tables and graphs.

INFLUENCE OF ACIDS AND SALTS IN SOLE LEATHER TANNAGE PART III—ACIDS AND SALTS IN THE EARLY TAN LIQUORS. H. Anderson, *J.S.L.T.C.* **41**, 1, 2, (1957). Previous work has shown a quantitative relationship, independent of pH and salt content, to exist between plumping and fixation of tan, thus giving experimental support to Braybrook's accessibility theory. The present experiments show that a similar relationship exists between plumping and firmness, but some evidence has been obtained suggesting that the plumpness of the grain layer fibres at the time of initial tannage influences the ultimate firmness of the leather to a degree out of all proportion to the relative depth of the grain and corium. Thus pH and salt content of the first few liquors in a yard have considerable influence on ultimate firmness.

THE INFLUENCE OF SMALL QUANTITIES OF OIL ON THE TENSILE PROPERTIES OF VEGETABLE-TANNED SPLIT HIDES. C. D. Pomeroy. *J.S.L.T.C.* **41**, 3, 106, (1957). Amounts of oil ranging from 0 to 32% have been added to degreased split hide leathers. Even small additions of oil (about 1%) are found to increase appreciably the tensile strength, breaking load, and percentage elongation at break. This result shows that small oil additions are sufficient to affect the interfibrillary adhesion, and supports the theory that the decrease in rate of abrasion of sole leather resulting from degreasing is due to the removal of the lubricants between the fibres.

CHROME TANNING

COMBINED USE OF MASKING AGENTS IN CHROME TANNING. Y. Inouye, Y. Oono, and Y. Fukui. *Bull. Japan Assoc. Leather Technol.*, **2**, 81-86 (1956). *Via. J.A.L.C.A.* **52**, 2, 101, (1957). The effects of adding Na formate, Na_2SO_3 , and Na phthalate, singly or in pairs, on fixation of Cr and Ts of leather were studied. A pH value from 4 to 5 is necessary to get high Cr fixation and Ts with formate liquors. At these pH values, Cr fixation in 48 hours declines slightly with increasing amount of formate but increases with increasing sulfite and phthalate. Ts does not always increase with increasing Cr fixation. Ts increases with the amount of formate and sulfite added, but declines with amounts of added phthalate. Phthalate and sulfite used together are more effective than either alone. The effect of formate plus sulfite is about the same as phthalate plus sulfite when the ratio of formate to sulfite is small. Formate plus phthalate is about as effective as phthalate alone. Aging lowers the tanning potency of phthalate-masked liquors. Formate masking produces fullness and softness; phthalate produced fullness; small additions of sulfite produce a smooth grain, but larger additions produce drawn grain. Phthalate liquors are stable at high pH values, but at too high pH values the leather shows drawn grain. (Note:—The tables in this article have English headings and are easy to understand).

THE INFLUENCE OF THE DURATION OF PICKLING AND METHODS OF CHROME TANNING ON THE PROPERTIES OF CHROME SIDE LEATHER. By M. F. Chambers, R. G. Mitton and E. F. Natrass. *J.S.L.T.C.* **41**, 2, 60, (1957). Chrome side leathers were made by use of a very short or a long pickle, by tanning with chrome liquors of various basicities, by adding all the chrome at the beginning of tannage or by adding only half then and the rest later, and were dyed with two different kinds of dye. The grease and chrome contents were determined and measurements made of area, thickness, density, resistance to compression, buckle-tear strength, dye penetration and colour fastness to rubbing. The outstanding result provide very clearly under the conditions of this experiment, is that thinner leather resulted from the short pickle, irrespective of the basicity of the tan liquor.

SOME CONSIDERATIONS ON BASICITY OF CHROME LIQUOR AS THE STANDARD OF CHROME TANNING. A. Kawamura and K. Wada, *Bull. Japan Assoc. Leather Technol.*, **2**, 71-80 (1956). (English summary). *Via. J.A.L.C.A.* **52**, 2, 101, (1957). The authors believe that the role of basicity in chrome tanning has been overemphasized. The amount of alkali ordinarily added in neutralizing has little effect on charges and complexly bound SO_4 content of Cr complexes. Merely heating $\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ solutions for 30 min. brings them to the same colloidal state as found in 33% basic, SO_2 -reduced Cr liquor. The structure of Cr complexes ("true" colloidal state, charge distribution, etc.) seems to be an important controlling factor in tanning.

OTHER TANNAGES

CHAMOISING EXPERIMENTS WITH PELT OF SUPERANNUATED SHEEP. Y. Sakimoto. *Bull. Japan Assoc. Leather Technol.*, **2**, 87-91 (1956). (English summary). *Via. J.A.L.C.A.* **52**, 2, 101, (1957). Fairly good leather was produced from skins of old sheep. Four different fish oils were used. The tanning capacity of the oil depended on its contents of unsaturated, oxidizable fatty acids as well as its I_2 value. No relationship was found between leather quality and so-called combined-oil content. The rate of replacement of water by oil in the skin had more effect on the rate of chamoising than chemical pretreatments of the pelt with HCHO , acids, bichromate, and chlorate.

THE TANNING CHARACTERISTICS OF ALIPHATIC ALDEHYDE-KETONE RESINS. By J. R. B. Hastings and T. White. *J.S.L.T.C.* **41**, 2, (1957). The alkali-catalysed reaction between aliphatic aldehydes and ketones provides condensates which can be resinated by further treatment with alkali. This provides the basis for a process of resin tannage consisting of: (i) impregnating hide with a suitable condensate (ii) resinifying the condensates *in situ* by alkali treatment. The method gives a range of light leathers, pale cream to yellow in colour, having shrinkage temperatures raised as much as 14°C and containing up to 20% of resin. Conventional methods of tannage can be applied if the condensates are converted to water-soluble resins containing sulphonic acid groups by treatment with alkali sulphites or bisulphites. Tannage with these products gives a range of light leathers, cream to orange in colour, having shrinkage temperatures raised as much as 50°C and having a degree of tannage of up to 60. The analysis of such solubilised resins by the

Official Method gives unreliable results. This can be shown by varying the time of contact with hide powder, the ratio of resin to hide powder, and the extent of acidification of the analytical solution. Like other sulphonated materials, these solubilised resins leach organic salt from the hide powder-afeature which can introduce as much as 5% error into the tannin estimation. The role of the sulphonate group in these solubilised aldehyde-ketone resins is discussed in relation to the results presented, and to published data on analogous sulphonated tanning materials. It is suggested that the products may have a certain potential value if used in conjunction with other tanning materials.

PROCESSES AFTER TANNING

IMPREGNATED SOLE LEATHERS. P. Champault, *Rev. Tech. Industr. Cuir*, 48, 125, 1956. *Via. J.S.L.T.C.*, 41, 3, 115, (1957). Properties of semi-chrome, impregnated semi-chrome, and rapidly vegetable-tanned sole leathers are compared. Water permeability and wear are shown to be superior in the impregnated semi-chrome to that in either of the other leathers. Details of the impregnation are not given. The author considers that impermeability is the main factor in the quality of sole leather, and that it contributes to its wear resistance.

DESMOPHEN-DESMODUR LACQUERS IN LEATHER FINISHING. W. Speicher. *Rev. Techn. Inds. Cuir*, 48, 161 (1956). *Via. J.A.L.C.A.*, 52, 2, 108, (1957). The film formation is made by chemical reaction of 2 components of relatively low molecular weight which by themselves are not film-forming but in drying form a polyurethane film of high molecular weight. The reaction is a polymerization of a di- or polyfunctional isocyanate (Desmodur) and a di- or polyvalent alcohol (Desmophen). Types of Desmodur and Desmophen as manufactured by Farbenfabriken Bayer are described as well as their application. Only solvents which do not react with isocyanate groups can be used, like esters, ketones, and aromatic hydro-carbons. For coloring, dyes soluble in organic solvents may be used. It is claimed that the use of Desmodur-Desmophen overcomes the disadvantages of linseed oil and nitrocellulose lacquers.

ADHESION OF FINISH TO UPPER LEATHER. G. L. Amos and G. W. H. Thompson, *J.S.L.T.C.* 41, 1, 23, (1957). An inexpensive method has been devised whereby the adhesive force of finish to side leather may be quantitatively measured. It is conveniently carried out by operators who are not highly skilled and gives good reproducibility. The test is suitable for routine checking of production lots, and is a valuable research tool whereby the effects of changes and modifications in processing and finish formulations may be quickly assessed. Very little damage to sides is incurred in sampling. Adhesion has been found to vary with position of sampling in any one side of leather. Types of binders degree of grain correct, nature of dyes, degree of retannage, ammonia concentration in bottom finishing layers and protein content of finish formulations have been found to have significant effects on the adhesion of finishes in various kinds of side leather.

THEORIES

STUDY OF THE AFFINITY OF BLACK WATTLE EXTRACT CONSTITUENTS PART IV RELATIVE AFFINITY OF POLYPHENOLS FOR SWOLLEN CHEMICALLY MODIFIED COLLAGEN. R. L. Sykes and

D. G. Roux. Column chromatography on various modified collagens, coupled with two-dimensional paper chromatography is used to study the qualitative effect of the chemical modification of collagen on the relative affinities of wattle tannin constituents. The polyphenols showed similar distribution patterns on each substrate. Taking into account the variable swelling of each substrate, the over-all affinities of the tanning constituents for the different substrates increased in order: esterified collagen, deaminised collagen, carboxymethylated collagen and acetylated collagen. These changes in affinity between substrate (various collagens) and adsorbate (wattle tanning constituents) were much less marked, and therefore probably less significant than inherent difference in the relative affinities of the individual polyphenols. The similarity in the relative affinities of wattle tannins for collagen modified collagens and also cellulose, conclusively establishes the predominantly hydrogen-bonding nature of the vegetable tanning process. The quantitative aspect of the tannin-collagen relationship is reviewed and discussed.

THE COMPOSITION OF EPIDERMIS. J. H. Bowes and R. G. Elliot. *J.S.L.T.C.*, 41, 3, 87, (1957). Epidermis has been separated from ox hide by means of treatment in warm water, and the amino acid composition has been determined. The majority of amino acid analyses previously reported for epidermis have been made on material obtained from abnormal sources, such as that from cornified areas and from subjects suffering from exfoliative dermatitis, and this is the first complete analysis of normal material which has been made. Epidermis is generally classified as a "pseudokeratin," and it differs markedly from the normal keratins, such as hair, in its much lower cystine content. It is now shown that its amino acid composition differs also in a number of other respects. The relative swelling and solubility of epidermis, hair, and wool in alkaline and sulphide solutions have been examined.

TESTING

STUDIES ON TANNINS, IV. ABSORPTION OF TANNIC ACID ON FORMALDEHYDE-UREA CONDENSATE AND ITS APPLICATION TO THE DETERMINATION OF TANNIC AND GALLIC ACIDS. Koiti Kimura, Sigeaki Kuwano and Hiroshi Hikino. *J. Pharm. Soc. Japan*, 75, 8, 962-966 (1955). *Via. Anal. Abst.*, 4, 1, 161, (1957). The use of the white condensate prepared from urea (40 g in 500 ml of water), formaldehyde (40% aq. soln. 50 ml) and N HCl (5 ml) was studied for the separation of tannic acid (I) and gallic acid (II). The sample soln. (5 ml) containing both I and II (each 5 mg) is treated with saturated NaCl soln. and the condensate (1, 0 g), then filtered and washed a few times with saturated NaCl soln. The filtrate and washings are combined and made up to 25 ml; a 10-ml portion is treated with ammonium molybdate (1%, 2 ml) for the colorimetric determination of II. The sum of I and II is similarly determined in the initial solution.

PENETRATION OF WATTLE TANNINS INTO HIDE AS EXAMINED BY CHROMATOGRAPHIC AND MOLECULAR METHODS. D. G. Roux and S. R. Evelyn. *J.A.L.C.A.*, 52, 2, 58, (1957). Chromatographic and molecular weight studies were made on each member of a set of wattle liquors used for tanning sole leather. There is an accumulation

ously circulated, a second circuit also being provided comprising a portion common to the first circuit and part of the feed supply of one component so that this component meets the first circuit in admixture with the reaction product, the other component being supplied to the first circuit at a point in advance of the second circuit. Apparatus illustrated and described is of particular application for the sulphonation or sulphatation of dodecyl benzene or a fatty alcohol with oleum or sulphuric acid. The process may also be applied to sulphophalogenisation with sulphuryl chloride. E. P. 697,244 is referred to.

PATENTS

TANNING WITH AMPHOTERIC SYNTANS. *Farbenfabrik Bayer.* Brit. Pat. 747,094. 1956. Via. J.S.L.T.C., 41, 2, 72, (1957). The amphoteric syntan is prepared by condensing 1-10 mol. of a polyvalent phenol with 1 mol. ammonia or aniline, and with an aldehyde. The syntan produced has maximum tanning properties near pH 7; it may be used alone, or before or after other tannages.

TANNING BY POLYALKYL ETHER DERIVATIVES OF SULPHONAMIDES. *Bohme Fettchemie G.M.B.H.* Brit. Pat. 748,995. 1956. Via. J.S.L.T.C. 41, 2, 72, (1957). Addition products of polyethylene oxide and sulphonamides (such as dodecylbenzene sulphonamide) are used as tanning agents; these may be applied previously to chrome tannage, or after formaldehyde. When applied together with a fish oil, a chamois-like leather is obtained suitable as clothing leather.

PRODUCTION OF CONDENSATION PRODUCTS OF UREA AND ALDEHYDES. *Deutsche Gold—Und Silber-Scheideanstalt.* Fr. Pat. 1,106,171: Rev. Tech. Industr. Cuir. 1956, 48, pt. 1. Via. J.S.L.T.C. 41, 2, 72, (1957). Urea or its homologues is condensed with saturated aldehydes (preferably formaldehyde) in an acid or alkaline medium in the presence of heterocyclic nitrogenous compounds having active methylene groups: such compounds are hexamethylenetetramine or others reacting similarly. The condensation may also be carried out in the presence of the constituents necessary for the formation of hexamethylenetetramine.

BODY COLOUR OR TOP FINISH FOR LEATHER. *Chem. Fab. Grunau.* E. P. 747,769. Through J. Soc. Dyers Cols., 1956, 72, 366. Via. J.S.L.T.C. 41, 2, 72, (1957). The product consists of a condensate of a soluble protein or protein decomposition products with higher fatty acids, resin acids, naphthenic acids, and/or higher aliphatic or aliphatic-aromatic sulphonic acids.

PROCEDURE AND COMPOSITIONS FOR THE TREATMENT OF HIDES AND SKINS BY ENZYMES. *D. Burton, R. Reed, and F. O. Flint.* F. Pat. 1,105,476, 1955. Via. J.S.L.T.C. 41, 2, 72, (1957). Hides and skins, either fresh or cured, are treated with mucolytic enzymes (defined as polygalacturonidase, elastase, pectinase, hyaluronidase, chondroitinase, amylase diastase, etc.) in buffer solution at pH 3 - 12.5. Proteolytic enzymes, mineral salts, and activating agents may be added. The treatment may be used to assist soaking back, for unhairing and dewooling, for bating, or for all three simultaneously. Skin so treated need not be

limed, and can be converted directly to gelatin or glue. Applied to chrome leather in the blue, more even fat-liquor penetration and dyeing are obtained.

METHOD OF PREVENTING SWELLING OF SKINS TREATED WITH ACID. *Elektrochemische Fabrik Kempen.* Ger. Pat. Appl. E9, 372; *Das Leder*, 1956, 7, 92. Via. J.S.L.T.C. 41, 2, 73, (1957). By the addition of formic, acetic, or lactic acid, the effect is increased which was described in Application E6, 708.

IMPREGNATION OF VEGETABLE-TANNED LEATHER WITH UREA-FORMALDEHYDE MONOMER. *P. E. Chambard and Institut De Recherches Pour Les Industries Du Cuir.* Fr. Pat. 1,104,978. Via. J.S.L.T.C. 41, 2, 73, (1957). Vegetable-tanned sole leather acquired increased resistance to water penetration and wear by treatment as follows: after tannage, the leather contains 10-30% water solubles; it is sammed to 40% water content. The leather is then drummed in a mixture containing 1-3% commercial urea - 3-9% formaldehyde (30%); the mixture must be freshly prepared. Drumming is continued until uptake is complete; then 0.2 - 0.5% oxalic acid (or 1-2% ammonium chloride) is added. The acidity produced effects polymerisation of the urea-formaldehyde monomer. The quantities given are expressed on the wet wt. of the leather. On completion of acidification, the leather is piled for 24 hr. dried, and finished in the usual way. The firmness of the leather produced is dependent upon the tannins originally employed.

1. G. M. Malim, S. 43, Jalan Bahry, Kulai, Johore, Malaya.
2. Mr. J. B. Ingram, India Leather Corporation, Madras.
3. Mr. E. Raghupathi, Mysore Chrome Tanning Co. Ltd., Bangalore.
4. Mr. R. Narayanaswamy, Messrs. E. K. M. & Sons, Erode.
5. Mr. B. S. Venkataraman, —do—
6. Mr. A. K. Das Gupta, M/s. Kapurthala Northern India Tanneries Ltd., Kapurthala.
7. Mr. M. Y. Malik Borha, Madras Chrome Tannery, Pallavaram.
8. Mr. K. H. Bhave, Western India Tanneries Ltd., Bombay.
9. Mr. M. Krishnaswamy, Chrome Leather Co. Ltd., Madras.
10. Mr. P. Sivaprakasam, —do—
11. Mr. K. M. Varughese —do—
12. Mr. M. S. Ramakrishnan, Light Leathers Ltd., Chromepet.
13. Mr. S. Sambasivam, M/s. Sreenivas & Co., Madhavaram.
14. Mr. K. Y. Gaitonde, —do—
15. Mr. M. G. Seshadri, Mysore Chrome Tanning Co. Ltd., Bangalore.
16. Mr. P. E. M. Krishnan, Ex-tanner, C. T. Ltd., Calcutta.
17. Mr. M. K. Hassan, M. M. Mohideen Thamby & Co., Madras.
18. Mr. R. S. Md. Abdul Khader, M/s. M. K. S. Mohamed Lebbai & Co., S. A. L. Tannery, Eluru.

RESEARCH BEARS FRUIT PRACTICAL DEMONSTRATION NO. 6.

Process: Manufacture of Box and Willow Uppers.

Period: 16th July to 5th August 1957.

Place: Central Leather Research Institute, Madras-20.

It is very gratifying for us to see that the tanners have taken kindly to our monthly activity in regard to the practical demonstration of processes developed at this Institute through research. A large number of tanners all over India are now taking full advantage of these demonstrations. The sixth in the series of practical demonstrations will be held between 16th July and 5th August 1957 on the manufacture of box and willow upper leathers.

Box and willow leathers are chrome tanned upper leathers meant for shoe uppers etc. The estimated production of this type of leather in India is about 55 million square feet annually and 20 per cent of this material is exported to a large extent to U.K. With the non-availability of the proper type of hides, difficulties have been experienced by the tanners to produce good quality chrome upper leathers from bad quality hides. Recognising the problems of the industry in India, the Central Leather Research Institute has worked incessantly in deve-

loping processes suitable for the indigenous conditions. Nine different processes have been so far developed and some of these have been published in the form of a bulletin. Two of the processes that have proved to be the best will be presently demonstrated.

With the increasing demand for the footwear industry in India, with the availability of the technical know-how and personnel and with the possibility of exporting finished leathers to other countries, the potentialities for this industry are obvious and every effort should be made to promote further growth of this branch of the industry, viz. manufacture of box and willow upper leathers.

If you are interested in this line of work, you are welcome to send your tanner-representative to actively participate in this demonstration from 16th July 1957 to 5th August 1957.

Arrangements have been made as usual at this Institute for boarding and lodging of the participants. Please let us know early the name of your representative who will participate in this demonstration.

A copy of the programme and the flow-sheet are enclosed for your information.

PROGRAMME

- 16th July 1957 : Soaking & Liming.
- 17th July 1957 : Liming.
- 18th July 1957 : Deliming, Bating & Pickling.
- 19th & 20th July 1957 : Chrome Tanning.
- 20th & 21st July 1957 : Piling.
- 22nd July 1957 : Sammying, Splitting if necessary and Shaving.
- 23rd July 1957 : Neutralisation, Dyeing & Fatliquoring.
- 24th July 1957 : Putting out, Sammying & Setting.
- 25th & 26th July 1957 : Drying.
- 27th & 28th July 1957 : Ageing in crust condition.
- 29th July 1957 : Sawdusting.
- 30th July 1957 : Staking, Ironing & Toggling.
- 31st July 1957 : Trimming, Buffing, Cleaning & Clearing.
- 1st & 2nd August 1957 : Seasoning.
- 3rd August 1957 : Glazing.
- 5th August 1957 : Ironing, Grading & Thus finishing.

FUTURE PROGRAMME

The Seventh in the series of demonstrations will be on Rapid tanning of E. I. kips and skins during August 1957.

C. L. R. I. NEWS

Dr. Y. Nayudamma, Assistant Director-in-charge, Central Leather Research Institute, Madras, has been nominated as Member of the Forest Utilisation Advisory Board of Madras State.

Dr. Y. Nayudamma, Assistant Director-in-charge, Central Leather Research Institute, has been nominated as a member of the Sub-Committee set up by the Leather Export Promotion Council, Madras, for evolving a scheme relating to the introduction of quality control of leather on a voluntary basis.

Dr. Y. Nayudamma, Assistant Director-in-charge, Central Leather Research Institute has been nominated as a representative of the Council of Scientific & Industrial Research on the reconstituted Research Committee of the Khadi & Village Industries Commission, Bombay.

Dr. Y. Nayudamma, Assistant Director-in-charge, Central Leather Research Institute attended the meeting of the Forest Utilisation Board on 27th May 1957 at Ooty.

Dr. D. Ramaswamy, Junior Scientific Officer, Central Leather Research Institute, Madras, has been deputed to the Indian Institute of Science, Bangalore to study the advanced techniques of Electrophoresis, Chromatography and Polarography.

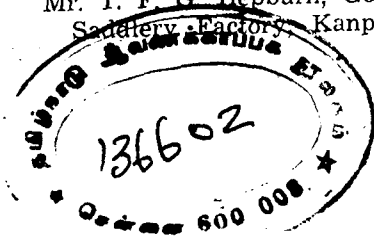
Shri K. S. Chandrasekaran, Junior Scientific Officer, Physics Division, has relinquished his post with effect from 3rd June 1957.

Dr. S. C. Dutta has been appointed as the Regional Liason Officer for the Madras Region and his headquarters will be at the Central Leather Research Institute, Madras 20.

Shri K. S. Jayaraman, Junior Scientific Assistant, Chemistry & Physics Division, has been awarded the M.Sc. degree by the Madras University for his thesis on "Neutralisation of chrome tanned leather".

VISITORS

Name	Date of visit.
Members of the Russian cultural delegation	14-5-1957.
Shri Santosh Singh, Planning Commission	22-5-1957.
Shri P. Battacharya, Indian Veterinary Research Institute, Izatnagar.	22-5-1957.
Mr. F. H. Hoek, FAO Expert, Government of India	22-5-1957.
Shri L. Sahai, Deputy Development Commissioner, Animal Husbandry, Government of India	23-5-1957.
Shri R. L. Kaura, Ministry of Food and Agriculture, Government of India	23-5-1957.
Mr. T. F. G. Hepburn, Government Harness and Saddlery Factory, Kanpur.	25-5-1957.



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