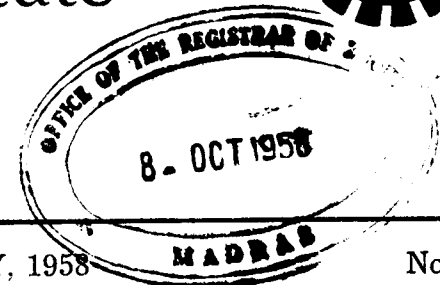


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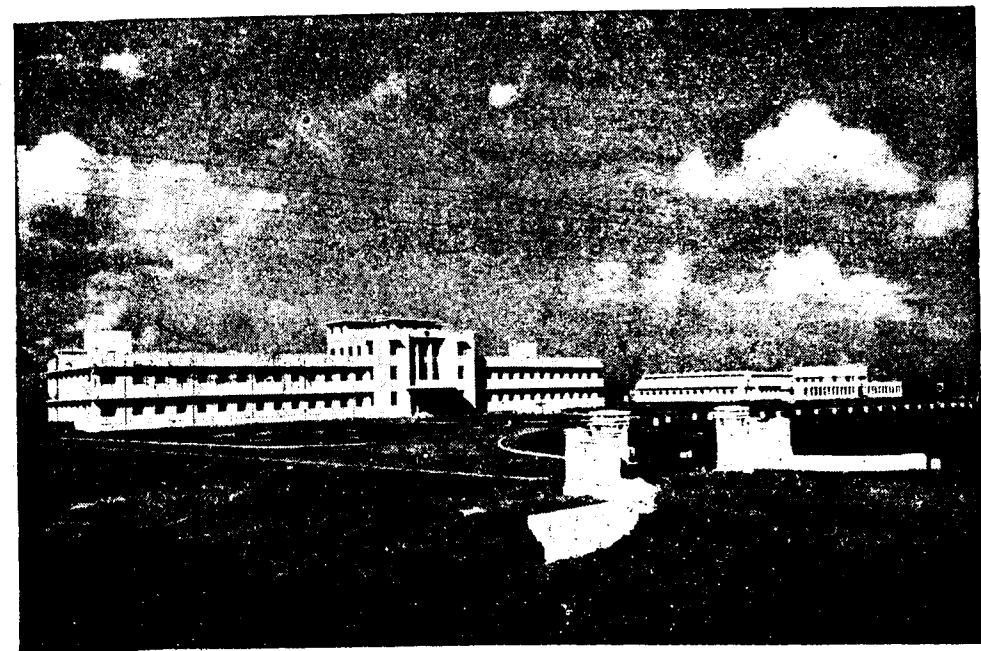


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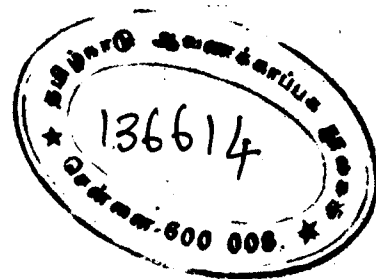
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SOLE LEATHER TANNAGE USING PITHECOLOBIUM DULCE BARK

BY

M. K. UDAYA VARMA, E. C. MATHEW & (late) B. M. DAS
Central Leather Research Institute, Madras

SUMMARY

Pithecolobium dulce bark singly and in blends with myrobalan has been tried for sole leather tannage. It has been found that a blend of Pithecolobium dulce bark and myrobalan in the proportion 5:1 gives a good solid sole leather of light colour.

The use of *Pithecolobium dulce bark* (Kodukapuli in Tamil, *Simachinta* in Telugu) in E. I. tannage has been already reported.¹ Because of its high tannin and moderate acid and salt contents, its suitability for sole leather tannage was investigated.

Preliminary experiments were conducted on small cut pieces of delimed buffalo hide (4" × 2"). Blends of the material with myrobalan in the proportion 4:1, 3:1 and 2:1 were used. It was found that sole leather of very good quality was obtained in all the experiments. So further experiments were carried out to find the most suitable blend for sole leather tannage.

Experimental

A wet salted buffalo hide was soaked in plain water and limed in once used lime liquor with 12% lime. It was unhaired on the eighth day, relimed using 12% lime, fleshed on the tenth day and left overnight in plain water. Next day it was delimed (1/3) with boric acid. The butt portion was cut into pieces (12" × 12") and the pieces for each experiment weighed.

Liquors for tanning were prepared by leaching as follows :—

- I. Pithecolobium dulce bark alone.
- II. Pithecolobium dulce bark and Myrobalan (5:1).
- III. Pithecolobium dulce bark and Myrobalan (4:1).
- IV. Pithecolobium dulce bark and Myrobalan (3:1).
- V. Pithecolobium dulce bark and Myrobalan (2:1).

The pelt pieces were drummed in 5° Bk liquor in each case for 15 — 20 minutes to give a uniform colour and then put in liquor of 7° Bk. The pieces were handled and the barkometer strength increased by 2° everyday, with beaming on the third day, till the barkometer of 45° was reached. After beaming, they were put in a liquor of 50° Bk, and 6 ozs. of the ground tanning materials were added to maintain the strength and the pieces kept in this for 3 days. Two more dusters were given at 55° Bk and 60° Bk, keeping the pieces in each duster for three days. They were then beamed and given two layers each of two weeks' duration, at 65° and 70° Bk. Table I gives the pH value of the tan liquors at the various stages of tanning.

TABLE I

pH Value of the Liquors at various stages of Tanning

Expt.		Bk.				
		5°	19°	50°	65°	Final
I.	Pithecolobium alone	5.45	4.45	4.5	4.8	5.1
II.	Pithecolob.+Myrob. (5:1)	4.5	4.7	4.35	4.3	4.5
III.	-do- (4:1)	4.4	4.45	4.1	4.0	4.1
IV.	-do- (3:1)	4.4	4.5	3.95	3.8	3.95
V.	-do- (2:1)	4.35	4.4	3.85	3.72	3.8

After completion of tanning, the pieces were piled for two days, and scrubbed well with a stiff brush and bleached by brushing with a solution containing 2% Perfectan 0 and 1% oxalic acid and then put in myrobalan liquor of 50° Bk. On the third day, they were beamed and put in another myrobalan liquor of 80° Bk. Next day they were beamed and oiled with Pungam Oil. A paste of 1% Epsom salt and 1% glucose was applied on the flesh side. The pieces were dried, set twice, seasoned and rolled.

A complete chemical, physical and microscopical examination of all the experimental leathers was done. The results are shown Table II, III and IV.

TABLE II

		I	Tan II	Liquor III	IV	V
Moisture	..	12.46	12.76	12.61	12.31	12.1
Oils and fats	..	7.34	6.43	6.02	8.23	9.36
Total ash	..	0.47	0.51	0.52	0.71	0.72
Soluble ash	..	0.47	0.49	0.51	0.57	0.7
Insoluble ash	..	—	0.02	0.01	0.14	0.02
Water soluble matter	..	11.85	11.66	10.44	13.23	12.8
Hide substance	..	38.44	38.65	37.92	34.7	34.7
Fixed tans	..	29.91	30.48	33.0	31.39	31.02
Degree of tannage	..	77.8	78.84	87.04	90.44	89.41
pH of water solubles	..	3.8	3.7	3.6	3.6	3.6
Shrinkage temperature °C	..	81.5	81.0	81.0	78.0	78.5
Yield of leather (%) (on delimed weight)	..	81.6	77.5	75.7	67.8	77.4

TABLE III

Tensile Strength

	Expt. No.				
	I	II	III	IV	V
(lbs./sq. in.)	3811	5568	4657	5281	5423

The abrasion strengths of the different leathers were tested using a Taber abrasion tester. The loss of weight in gms per 5,000, 10,000, 15,000, and 20,000 revolutions was found.

TABLE IV

Expt. No.	Loss of Wt. in gms. per			
	5,000 revs.	10,000 revs.	15,000 revs.	20,000 revs.
I	1.388	2.229	2.922	3.547
II	1.041	1.816	2.533	2.983
III	0.813	1.570	2.294	2.826
IV	0.750	1.453	2.026	2.726
V	0.713	1.758	2.618	3.017

Microscopical Observations

Experiment I: Fairly full bundles and less than fairly compact weave with less than medium angle. Very large amount of splitting.

Experiment I: Fairly full bundles and fairly compact weave with less than medium angle. Large amount of splitting.

Experiment III: Fairly full bundles and more than fairly compact weave with medium angle. Large amount of splitting.

Experiment IV: Slightly thin bundles and less than fairly compact weave with low angle. Large amount of splitting.

Experiment V: Fairly full and fairly compact weave with low angle. Very large amount of splitting.

Tannage with *Pithecolobium dulce* bark alone has produced a satisfactory solid sole leather of good colour. Blend-

ing of myrobalan has lightened the colour of the leather. The leathers in experiments IV and V were rather less firm than the others.

According to the microscopical assessment the best leather is produced in Experiment III and the next best in Experiment II. Abrasion resistance is progressively increased as myrobalan is increased in the blend. Tensile strength of leather of Experiment I is quite low whereas it is high for those of Experiments II & III.

On the whole leathers produced in Experiments II and III were found to be the best in the series. To find how these leathers compared with wattle — myrobalan tanned sole leather, experiments were repeated using these blends.

A green buffalo hide was washed well, limed, unhaired, relimed and fleshed as in the previous experiment and cut into two halves. Two pieces (16" × 16") taken from the butt portion of each half were weighed and 1/3 delimed with boric acid. The left halves were tanned in a liquor obtained by leaching wattle bark and myrobalan (4:1) whereas the pieces from the right half were tanned as follows:

- I. With a blend of *Pithecolobium dulce* + Myrobalan (5:1).
- II. With a blend of *Pithecolobium dulce* + Myrobalan (4:1).

Tanning, myrobing, etc., were done as described in the previous experiment.

A complete chemical, physical and microscopical examination of the experimental leathers and control was done and the results are given in Tables V to VIII.

From a microscopical examination, the control leathers appear to be more compact and comparatively better structured than the corresponding experimental pieces. In ex-

perimental leather II the opening up of the fibre bundles or splitting appears to have been effected a little more than in the control. The comparatively loose structure in the case of the experimental leathers may be due either to greater opening up of the fibre bundles or to less deposition of tans and nontans. This is supported by the lower degree

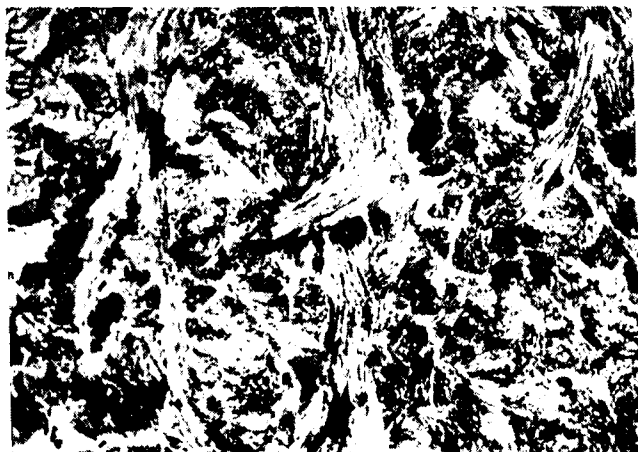


Fig. 1. Expt. I. P.D. + Myrob (5 : 1)

of tannage of these leathers compared to the control. The fibres in the case of experiment I appear to be rather fuller than its control. For sole leather, experimental leather I is better though experimental leather II is also not bad. The nature of splitting up and angulation found in experimental leather II appears to be suitable for harness leather. (Photomicrographs are given):

TABLE V

Tensile Strength

	Expt. I	Control	Expt. II	Control
(lbs./sq. in.)	5509	5839	5263	5194

TABLE VI
Abrasion Tests

		Loss of wt. in gms. per	
		5,000 revs.	10,000 revs.
<i>I. Taber Abrasion Tester</i>			
Expt. I	..	0.493	0.959
Control	..	0.308	0.694
Expt. II	..	0.525	0.926
Control	..	0.323	0.670
<i>II. Rubber Abrader</i>			
		332 Loss in thickness for	
		100 revs.	200 revs.
Expt. I	..	0.048"	0.0675"
Control	..	0.042"	0.061"
Experiment II	..	0.053"	0.071"
Control	..	0.0485"	0.068"

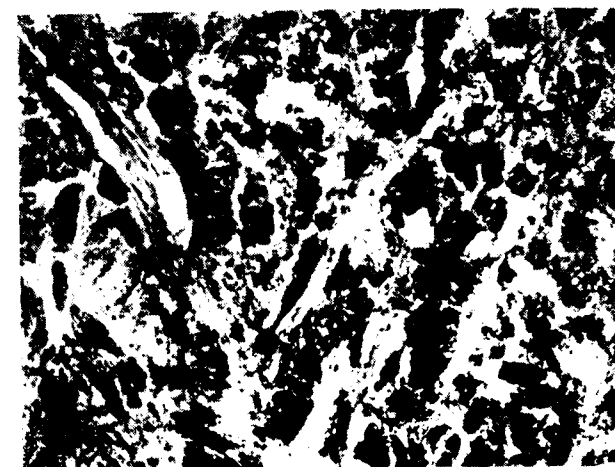


Fig. 2. Control for Expt. I

TABLE VII

Kubelka water absorption

		% absorption in 24 hours	% absorption in 24 hours
Expt. I	..	43.16	50.36
Control	..	35.10	43.85
Expt. II	..	49.30	56.78
Control	..	36.94	47.20

TABLE VIII

Chemical Analysis

		P.D. + Myrob. 5:1	Control	P.D. + Myrob. 4:1	Control
Moisture	..	13.33	13.67	12.91	12.94
Oils and Fats	..	2.81	2.11	4.26	4.43
Total ash	..	0.95	0.70	1.10	0.96
Soluable ash	..	0.56	0.54	0.62	0.34
Insoluble ash	..	0.39	0.16	0.48	0.62
Water sol. matter	..	9.74	10.20	11.94	12.69
Hide substance	..	43.20	42.85	41.01	39.29
Fixed tans	..	30.53	31.01	29.40	30.03
Degree of tannage	..	70.66	72.38	71.68	76.42
pH. of water soln.	..	3.95	3.95	3.95	3.95
Shrinkage temp.	..	79°	82°	79°	78°
Yield of leather					
(on fleshed wt.)	..	65.60	70.90	70.80	71.50

Resistance to abrasion. Abrasion tests were carried out both by using a Taber abrasion tester and a rubber abrader.

Conclusion. The experimental leathers are of very light colour. They are quite solid. Compared with the con-



Fig. 3. Exp. II P.D. + Myrob (4:1)

trol, tensile strength is almost the same, but resistance to abrasion found by two different methods, is less. Water absorption is also geater for the experimental leathers.

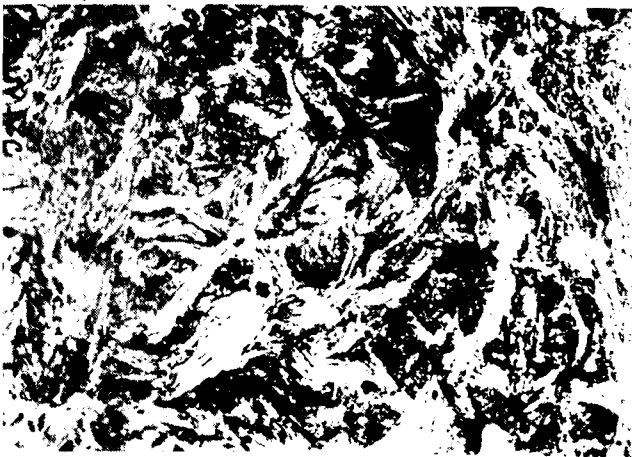


Fig. 4. Control for Expt. II

Leather tanned with 5:1 blend of Pithecolobium dulce and Myrobalan has a greater tensile strength, greater resistance

to abrasion and absorbs less water than leather tanned with a blend of 4 parts *Pithecolobium dulce* and 1 part myrobalan. Microscopically also, sole leather in Expt. I is definitely better. So it may be concluded that for manufacture of sole leather a blend of five parts *pithecolobium* with 1 part myrobalan is the best. As this sole leather also compares favourably with the wattle-myrobalan tanned sole leather, this material may be advantageously utilised for replacement of wattle in sole leather tannage.

The author's thanks are due to Sri S. K. Mitra for the microscopical assessment and photomicrographs.

REFERENCE

M. K. Udaya Varma, E. C. Mathew and B. M. Das, *Bull. C.L.R.I.*, 2, 204 (1956).

RESEARCH BEARS FRUIT

Practical Demonstration No. 3

(Second Series)

Manufacture of Glazed Kid Leather by combined one and double bath tanning method with indigenous materials

Process No. 2 *

BY

J. C. DEB and G. N. HORE

Raw material : Wet salted (Erode) prime quality goat skins of average size 30" to 32" are taken.

Soaking : The skins are soaked for 1½ hours to 2 hours in plain water. They are then taken out, trimmed, broken over the beam on the flesh side by a blunt knife and washed thoroughly in running water for 1 to 1½ hour to remove the salt. The skins are taken out, drained and weighed for liming.

Liming : Liming is done first with a depilating paste and then in a lime liquor in a paddle as follows :—

A sodium sulphide solution of 12°Be, or 90·5°Bk, i.e., sp. gr. 1·091 is made. To this, lime is added till the mixture becomes a paste. For a pack of 100 skins, about 7 to 10·5 lbs. of sodium sulphide, 26 to 39 lbs. slaked lime and 40 to 60 lbs. of water, are required to get a paste of necessary consistency.

The paste is applied on the flesh side of the skin in the evening, say at 4 P.M. and the skins piled on the floor, flesh to flesh and left overnight. Next morning the skins

* Process demonstrated in June 1958.

are unhaired, and washed with $\frac{1}{2}\%$ ammonium chloride on the soaked weight of the skin in a drum or paddle with sufficient float of water, just to remove the excess of sulphide from the skins; the drum is run for 10 to 15 minutes.

The skins are then put in a paddle containing 8 to 10% lime and sufficient float of water, i.e., 300 to 400% water on the soaked weight of the skins and left there for three days. The skins are paddled in the lime liquor for 10 to 15 minutes each time, thrice every day — in the morning, at noon and in the evening. On the 4th day the skins are scudded, fleshed and then weighed for deliming and bating.

Deliming: The skins are then delimed with
Ammonium chloride: $\frac{1}{2}$ - $\frac{3}{4}\%$ on the fleshed weight.
Water: 200-250% -do-

The skins are run in the deliming bath in a drum for half an hour and then washed in plain water and are ready for bating.

Bating: Overnight bating method is followed. The delimed skins are bated in a covered paddle using the following composition:

C.L.R.I. bate No. I: 1 to 1.5% on the fleshed weight.
Water: 300 to 350% -do.-

The bath is prepared with half the quantity of bate using water at room temperature and the skins are paddled in it for one hour and left overnight in the bath. Next morning the remaining half of the bate is added and the temperature of the bath is raised to 100.4°F. by passing steam. The skins are paddled in the bath keeping the temperature of the bath at 100.4°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.

Bating can be regarded to have been satisfactorily completed if (1) the cut section of the bated pelt is not coloured

red with phenolphthalein, (2) the bated skins are quite fallen and flaccid and retain thumb impression, (3) the scud comes out easily when the bated stock is scratched with finger nail, (4) air can be forced through the pelt and (5) the adhering flesh can be removed by scratching the flesh side with finger nail.

After completion of bating, the pelts are taken out, scudded well, washed in cold water of 86° to 90°F, and immediately pickled.

Pickling: For pickling the following composition is used:

Salt: 8 to 10% on the fleshed weight.
Water: 75-100% -do-
Hydrochloric acid: 2-2½% -do-

The bath is made with the above chemicals in a drum. The bated stock is put into it and the drum run for one hour; the stock is left in the bath overnight. Next morning the skins are drummed for half an hour, taken out and horsed up for sometime and then taken up for tanning. The pickle liquor is preserved for use later in the process.

Tanning: Tanning is done by the combined single and double bath process. The chrome liquor used for single bath tanning is made as follows:

Bichromate of soda: 10 lbs.
Sulphuric acid (sp. gr. 1.84): 9 lbs.
Molasses: 4 lbs.
Water sufficient to make up 11,000 c.c.

Basicity is adjusted to 96.4 (Procter). The pH of the liquor will be 2.9 to 3.

The pickled pelts are taken in the tanning drum containing 100 % water on the pelt weight and the first instalment of the above chrome liquor is added. Altogether chrome liquor equivalent to 2% bichromate of soda on the fleshed weight is added in 4 equal instalments at intervals

of 30 minutes and the drum is run for half an hour more. Then the preserved pickle liquor from the pickle drum is added and the drum is run for one hour more. Now 3 % bichromate of soda on the fleshed weight of the skins in 25% water is added to the drum in 6 equal instalments within the period of half an hour. The drum is run for 2½ hours more and left in the bath overnight. Next morning the stock is drummed for 30 minutes and then the bath is drained; the skins are put in the reducing bath made as follows : —

Hypo: 4% on fleshed weight.
Water: 100% -do-

The skins are run in the above reducing bath for half an hour. Then 6% hypo in 50% water and 5% hydrochloric acid in 50% water are added in 5 equal instalments at intervals of 30 minutes. For each instalment, the two solutions are mixed together just prior to addition into the drum. The drum is run for 3½ hours more. The pH of the tanning bath is adjusted to 3·5—4·0 before unloading. The leathers are then subjected to the boiling test. They are then washed for 10 minutes by diluting the reduction bath and piled up on the platform for 2 to 3 days to drain off the excess of moisture.

Sammying and shaving : The leathers are then slicked or struck out on the flesh side, sammed, shaved and weighed for neutralisation, dyeing and fatliquoring.

Neutralisation : The skins after thorough washing in a single change of water are neutralised for half an hour with sodium bicarbonate solution of the following composition.

Sodium bicarbonate: ½% on the shaved weight.
Water: 200% -do-

The bath is made in a drum at room temperature. The skins are put into it, worked continuously for half an hour and then tested with bromo cresol purple. Proper neutrali-

sation is indicated by purple colour on the leather surface and yellow colour in the middle layer of the leather. The skins are then taken out and washed twice with plain water. They are then ready for dyeing and fatliquoring.

Dyeing and fatliquoring : For dark brown shade the skins are dyed with the following composition :

Acid orange:	½%	on the shaved weight.
Naphthalene leather brown ADS:	¾%	„
Naphthalene leather brown GRS:	1%	„
Comassic blue:	1%	„
Formic acid:	¼%	„
Water at 130°F:	200%	„

Before putting in the dye bath the leathers are first drummed for 10 minutes in water at 104°F to attain that temperature. The conditioned leathers are then put grain side out into the drum containing 200 % water at 130°F. All the dyes are dissolved together in a bucket, and the solution is strained through a piece of clean cloth into another clean bucket, and half of the dye solution is put into the rotating drum through hollow axle and the drum run for 15 minutes and then the other half of the dye is put in. The drum is run for another 15 minutes. Formic acid is added and the drum run for 10 minutes.

The leathers are then fatliquored in the same bath with the following composition based on the shaved weight of the leathers for 30 to 45 minutes at 130°F.

Sardine fish oil (foots free):	1%	on the shaved weight.
Castor oil:	1%	-do-
Sulphated fish oil:	½%	-do-
10% soap solution:	½%	-do-

pH of the fat liquor emulsion is adjusted to 7·8—8·0. Then 3 % cutch extract dissolved separately is added to the exhaust fatliquor bath and the drum run for 10 minutes. The leathers are then taken out and horsed up overnight.

Striking out and oiling up: Next day the leathers are struck out on the flesh and grain sides. A mixture of one part foots free fish oil and two parts kid finishing oil is then applied on the grain side and the leathers hung up in the shade for sammying.

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

Finishing.

(a) *Sawdusting, staking and buffing:* The dried skins are stored for some days for conditioning. They are then 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 each containing one dozen skins, overnight. Next morning the skins are staked again by the same machine with considerable pressure. They are then aired off a little and buffed on the flesh side with buffing machine using 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) *Staining, seasoning and glazing:* The skins are first stained with

10% acetic acid solution: 1 gallon.

Bismark brown: 1 oz.

The stain coat is applied on the grain side by a brush, dried and then given two successive bottom season coats on the grain side with the following bottom season.

Bottom Season :—

C.L.R.I. tan pigment: 10 ozs.

„ black pigment: 2 ozs.

Neeran brown orange dye: 7 gms.

Nap. Leather brown ADS: 7 gms.

Milk or 7½% Casein Solution: 10 to 12 ozs.

Ox blood: 8 ozs.

C.L.R.I. binder M.G.: 4 ozs.

T.R.O. binder: 1½ ozs.

C.L.R.I. glazing finish: 8 ozs.

Ammonia: 1 oz.

Water to make one gallon.

After applying two successive pad coats, the leathers are dried, glazed and then given a top season coat.

Top season coat:

Bottom season: 2½% lbs.

C.L.R.I. binder M.G.: 4 oz.

„ glazing finish: 8 ozs.

Milk: 12 ozs.

Formaldehyde: 6 ozs.

One pad coat and spray coat on the grain side are given. The following fixing coat is then sprayed.

10% Casein solution: 1 part.

Formaldehyde (40%): 1 part.

Water: 6 parts.

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

Final glazing: Inclined bed glazing machine is the best. First glazing is done under heavy pressure moving the skin all round. The glazing produces glass marks on the grain which are smoothened out by glazing under light pressure, the second time. The glazing is skilfully done without producing pleats.

Measuring, smooth plating, ironing, grading and packing: The glazed skins are then measured and smooth plated with 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.

N.B.: *Wherever possible, only the indigenous materials are used:*

IMPROVEMENTS IN CURING AND PRESERVATION OF SKINS AND HIDES*

BY

S. C. NANDY, S. N. SEN and (late) B. M. DAS

SUMMARY

A substitute for Khari salt has been developed. This mixture of sodium sulphate, magnesium sulphate and a little ammonium sulphate, absorbs much less moisture from the surrounding atmosphere even in highly humid conditions and inhibits the growth of harmful bacteria. This is a clean salt mixture and naturally does not permit adulteration by plastering mud along with curing salt. The preservative efficiency of this mixture and the quality of leathers produced from skins so treated, are comparable to those obtained with Khari salt. The addition of sodium sulphate and ammonium sulphate has been found to increase the bacteriostatic action of common salt even at high R.H. values. The growth of red halophilic organisms also is appreciably checked.

Curing is an operation necessary to preserve raw hides and skins in a sound condition till they are taken up for tanning. The time lag between flaying and tanning is anything from a few hours to several months (in the case of hides and skins exported to other countries). So, uniform efficiency under a varying conditions of humidity and temperature is an essential requirement of a curing agent. Also, it should be able to inhibit bacterial action, the main cause of deterioration of raw hides and skins.

In India the traditional methods of curing are drying, dry-salting and wet salting. The first two methods are employed with stock intended for export while the hides and skins to be used locally are cured to a very large extent by the third method.

* These processes, originally covered by Ind. Patents Nos. 56251 and 57886, are now released to the trade free of cost.

Drying. This method is disadvantageous because dried hides and skins are not easily soaked back to their original moisture content. Moreover, drying, if not carried out properly leads to defects like sun-blisters. Damage during storage by insects also is associated with this type of curing. So, curing by drying is not very popular in this country and is resorted to in the interior villages only.

Dry-salting. Dry-salted hides and skins are in contrast to dried ones not difficult to soak back provided of course the right type of curing salt has been used. Common salt which is used for wet-salting cannot be advantageously used for dry-salting because of its hygroscopic nature. Innes¹ has shown that at 80% relative humidity the hygroscopic nature of sodium chloride becomes very marked. Temperature also has been shown to have a pronounced effect on the degree of moisture absorption by sodium chloride. In this country marine salt is generally used for curing and this material contains impurities like calcium and magnesium salts and usually a number of harmful halophilic bacteria also. Temperature and humidity conditions vary in India from region to region and from season to season. Storing dry-salted stock cured with common salt at a relatively high R.H. would lead to absorption of atmospheric moisture by the hides and skins and this would allow growth of red heat and other salt tolerant organisms. So for dry-salting, a saline earth known as Khari salt is commonly used in regions having high temperature and humidity. This material is very efficient in maintaining the cured hides and skins in a good condition for a considerable time. However, even this salt has some draw-backs:

Being an earthy efflorescence, it is mixed with considerable amount of earthy matter. On account of this, stock cured with Khari salt is inclined to be heavily plastered; dry-salted material is usually sold by weight and scope for increase in weight by loading is great, leading to complaints from buyers against Khari-salted stock. Khari salt may con-

tain as impurities, iron salts, which would produce stains in leather. Further, production of this salt is restricted to a small area, namely some districts in Bihar State; so its supply is limited and cannot cater to the great demand for it in other parts of the country.

So the need for a clean substitute for Khari salt, possessing its good curing properties, but devoid of scope for adulteration, has been felt for a long time. The following salts which could be possibly used as curing agents have been investigated as regards their properties..

Sodium sulphate. Thomas and co-workers² carried out investigations on the deleterious effect of certain neutral salts on hide substances. It was found that while all the halides could bring collagen into solution, sulphates and thiosulphates did not peptise collagen. Treatment of collagen with saturated solution of sodium sulphate for a long period of 170 days at 37°C did not result in any break-down of collagen, whereas the loss was more than 30% with a blank kept in water covered with toluene. When treated with a molar solution of sodium sulphate, collagen takens in only a small quantity of salt; on the other hand the protein is dehydrated. Also the shrinkage temperature of the original fibre is slightly increased and not lowered. Anhydrous sodium sulphate has been shown to absorb moisture at R.H. greater than 70%, the absorption continuing till the salt was completely hydrated. After formation of the decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), there is no further absorption even at higher R.H. values. According to Bleeck³ dry-salting with sodium sulphate has the following advantages over the other methods of curing: No loss of substance, pliability and less moisture absorption. Because of these advantages, sodium sulphate has been recommended^{4, 5} for curing hides and skins, especially for dry-salting in humidity conditions. Das, Dhavale and Pal⁶ recommended use of a mixture of 5 parts of anhydrous sodium sulphate and .1 part of sodium chloride for dry-salting.

Magnesium sulphate. This salt also has been shown to have not much peptising effect on collagen, the effect being less than that of pure sterile water. The hygroscopicity of magnesium sulphate has been shown to be,^{1, 7} much less than that of sodium sulphate even at cent per cent R.H. Weir and Carter⁸ have from their studies on the effect of neutral salts on shrinkage temperature indicated that magnesium sulphate might be a better curing agent than sodium chloride.

Ammonium sulphate. This salt does not have any specific value as curing agent, however it has been shown to be effective to some extent in preventing the growth of red heat organism.⁹ This may be due to its action in lowering the pH of salt mixtures. Stuart and Fry¹⁰ have shown that growth of halophilic red heat organism was inhibited in brines having pH value of 5.0.

Experimental. Equipped with the information on the properties of these salts, several salt mixtures of composition given below were made and hide pieces were cured with them. After a long period of preservation the cured test pieces were tanned and finished and the quality of leather was adjudged.

From a preliminary evaluation the following salt mixtures were considered better and experiments were repeated and the results compared with those got with Khari salt.

- | | |
|----------------------|-------------|
| (i) Sodium sulphate | — 70 parts. |
| Magnesium sulphate | — 20 „ |
| Ammonium sulphate | — 10 „ |
| (ii) Sodium sulphate | — 35 parts. |
| Magnesium sulphate | — 40 „ |
| Ammonium sulphate | — 25 „ |

- (iii) Sodium sulphate — 45 parts.
- Magnesium sulphate — 50 „
- Ammonium sulphate — 5 „
- (iv) Filtered Khari salt.

Freshly slaughtered cow hide was washed well and lightly fleshed; the experimental pieces were cut from the butt position of this hide. These were then cured with 15-20% of the salt mixture calculated on the green weight. The required amount of salt mixture was then applied on the hide pieces as a saturated aqueous solution two or three times. Next day the pieces were nailed on boards and allowed to dry up in the shade. These were kept under observation for a period of four months.

Results.

Mixture (i). The cured pieces were dry and hard; they soaked well after proper soaking and became soft; during liming, swelling and water uptake was considerable. Leathers obtained were soft, round in feet and resilient. Tearing strength was high.

Mixture (ii). The cured pieces although dry, absorbed moisture in humid condition; they became soft on soaking. In liming, swelling was more than with Mixture No. (i) and the water uptake was maximum. The final leathers were full, soft and round but slightly loose. Tearing strength was satisfactory.

Mixture (iii). The cured pieces were perfectly dry, became soft on proper soaking; swelling and water uptake during liming was less than with Mixture (ii). The leathers were very full, plump and round while the grain was smooth. Tearing strength was satisfactory.

Mixture (iv). The cured hide pieces were dry and hard considerable time required to soak back properly. They

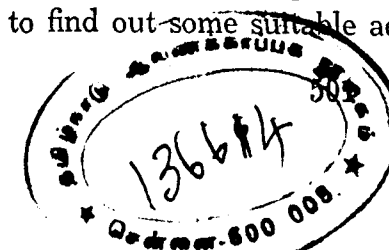
swelled well and the water uptake was considerable. The leathers produced were soft, round and full. Tearing strength was high.

The above experiments show that all the curing salt mixtures tried in this experiment give a satisfactory cure and preservation compared to ordinary Khari salt. Mixture No. (iii) seems to be slightly superior and was later tried for curing goat skins. It has been observed that goat skins cured with this mixture could be preserved for about 8-10 months; the leathers obtained with the stock cured for this period were as good as those cured with Khari salt, if not better. As mentioned earlier, use of ammonium sulphate is intended to bring the pH of the salt solution slightly to the acid side. If the pH of the mixture of salts of sodium sulphate and magnesium sulphate is near about 6.0, addition of ammonium sulphate is not necessary. It should however, be noted that, the composition of salt mixtures tried in these experiments, is not rigidly fixed; it may have to be varied depending upon temperature and humidity conditions.

The tanner prefers wet-salted stock to dry salted or dried stock because of easy soaking back and the possibility of evaluating the hide from different physical and chemical considerations. Common salt is extensively used for wet-salting hides and skins. It is however, known that common salt has got a limited bacteriostatic action and preserves hides or skins in Indian conditions for a period of about 6 or 7 weeks after which hair slip develops. High humidity and temperature may shorten this period further. Moreover, common salt produced from marine sources usually contains a large number of red halophilic organisms which gradually develop patches on the hide or skin surface.

Owing to this limitation in the use of common salt various attempts are being made in various parts of the world to find out some suitable adjuncts, which when used

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along with common salt would increase the bacteriostatic and preservative efficiency of common salt.

In an attempt to improve the curing efficiency of common salt in wet-salting, the abovementioned salts (ammonium sulphate, sodium sulphate and magnesium sulphate) were tried in admixture with common salt, and the following composition was found to improve the curing efficiency to a considerable extent.

Sodium chloride : 40-50%

Sodium sulphate : 35-40%

Ammonium sulphate : 10-20%

Commercial varieties of the chemicals were taken according to the above proportions, mixed well, and then 30% of the above mixture, calculated on the green weight of the hide, was applied. The procedure was the same as that with common salt. This mixture is suitable for use in comparatively higher humidity and if the humidity of the surrounding atmosphere is not so high, the salt mixture composition can be adjusted by increasing the proportion of sodium chloride.

This mixture greatly improves the preservative efficiency of common salt by preserving the cured stock for a period of 12 weeks or so. This may be partly due to the fact that, this salt mixture does not absorb so much moisture from the atmosphere and hence indirectly checks bacterial growth. Growth of the red halophilic organisms also was greatly suppressed when cured with this salt mixture.

It is however, true that addition of bactericides like sodium pentachlorophenate or parachloro metacresol, etc., to common salt might be much more advantageous, but due to the non-availability of these materials in India so readily, these were not tried in the present work. The aim has been to improve the curing efficiency of common salt by mixing other easily available salts of commercial quality, so

that the advantage gained through higher curing efficiency was not counteracted by increased cost.

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TECHNICAL SEMINAR

Leather Industry in Bombay State*

BY

Y. NAYUDAMMA

In active co-operation with the staff of the Small Industries Service Institute, a number of tanning and leather goods centres in the Bombay State covering Poona, Satara, Bombay and Ahmedabad have been visited.

From what has been seen, the industry can be divided into the following branches: (i) Raw hides dealers and merchants, (ii) Bag tanners in the village, (iii) E. I. tanners, (iv) Industrial leather manufacturers, and (v) Leather goods manufacturers. Just as Madras is famous for the E. I. tanning industry, Bombay is a region famous for the manufacture of industrial leathers and leather goods. Some of the problems of these various sectors of the leather industry are given below:—

(i) *Raw hides and skins dealers*: Due to the very bad flaying, an acute shortage of good quality raw hides needed for the manufacture of industrial leathers is felt. Plastering with mud and clay has been noticed in the cottage and small-scale sectors. Some of the ware-houses exporting large quantities of skins in dry as well as wet salted condition have kindly agreed to co-operate with the Central Leather Research Institute by giving us various types of defective skins for our study.

(i) *Bag tanners*: Bag tanned sole leather appears to be an important sector in the leather industry of the state,

*Condensed from the talk given on 6-6-1958.

the important regions being, Satara, Kolhapur and Sholapur. The leather is tanned by the usual method covering two limings (no deliming), colouring and tanning in bags with blends of myrobalan and babul. The leather so produced is soft and the yield is around 50% on fleshed weight. The conditions under which this bag tanning is operated in the villages really merit considered thought for their improvement. Some of the bigger and famous units in Poona and Satara produce good quality sole leather, light in weight and having good colour. These tanners do not like to get additional weight in the leather as it gives less cutting area and is difficult to be operated by the village cobbler. A re-tanning centre has been set up by the Government of Bombay to introduce retanning of the bag tanned leathers as well as to introduce pit tanning of sole leather. The introduction of C.L.R.I. techniques in this centre should prove helpful. It is gratifying to note that some of the bag tanners have shown keen interest in sending their men for advanced training at the C.L.R.I. The Government of Bombay has also given encouragement to these tanners by introducing certain amount of bag tanned leather in the manufacture of shoes meant for police and forest departments.

(iii) *E. I. Tanners*: The E. I. tanners in Bombay State appear to be tanning a large amount of goat and sheep skins but not much of kip except in a few centres. Leathers produced here are not up to the mark as compared to the ones tanned in the Madras State, the inferior quality being probably due to lack of proper technique, particularly in the process of Elangaram, etc., and dearth of suitable tanning and raw materials. Moreover these leathers are mainly intended for finishing within the State itself; a portion only is exported. Most of the labour in these E. I. tanneries hails from Madras. So evidently, the different types of water, climatic conditions, methods and materials available in this region are responsible for the failure to produce the same quality of E. I. leather.

Some tanners have shown interest in the activities of the C.L.R.I. and have asked for permission to send some of their men to the Institute to learn the newer techniques. The Small Industries Service Institute has also agreed to demonstrate some of these techniques in their tanneries.

(iv) *Industrial Leathers*: A variety of industrial leathers such as raw pickers, picking band, lace, loom leathers, etc., and also certain hydraulic leathers, ram rings, washers, are made in the vicinity of Bombay in both organised as well as small scale tanneries; the pickers and picking bands, particularly pickers, are concentrated in Ahmedabad. The major problem that seems to face this group is the lack of steady supply of good quality raw hides. Some of them are importing large quantity of hides. A substitute for sperm oil and having to use poor hides are the main problems of the pickers manufacturers. Further the pickers needed for the automatic looms are different from those for the ordinary looms. Researches may be undertaken in our Institute on these problems.

In the case of picking band manufacturers, substitutes for quebracho extract and cod oil, the need for good quality sardine oil from the West Coast, and for good quality raw hides, are the major problems. Some of these tanners have agreed to send their technologists to watch some of the modern techniques of manufacture of picking bands at the Central Leather Research Institute.

(v) *Leather Goods Manufacturers*: A meeting of the Leather Goods Manufacturers and Dealers Association provided an opportunity to acquaint them with the activities of the C.L.R.I. and also to learn their problems. The problems that face this industry appear to be that the quality of finished leathers supplied to the leather goods manufacturers is deteriorating, the measurements of the leathers supplied being wrong; the chemicals and other auxiliaries that go into the making of leather goods are not available

in sufficient quantity. Many of these manufacturers have been fully satisfied with the latex cement made at the Central Leather Research Institute and they want more of this material to be supplied in bulk quantities. There are also problems related to the adhesion of the enamel lacquer pigments on the leather surface and also the non-availability of frames, etc., for the manufacture of leather goods. The C.L.R.I. should set up works to supply the leather goods industry with the requirements like adhesives, polishes, stains, etc.

The All-India Khadi and Village Industries Commission Centre at Borivli also was visited. The items attracting one's attention at this centre are the decolorisation of neem and other oils by simple sun-bleaching and the utilisation of bones as bone manure and of cow dung, in preparing gas.

Here, there is a small tannery preparing sole leather for making leather goods. The centre has also contract with the Aarey Milk Colony for getting all the animals dying there, for flaying and for utilisation of carcass.

The question of how best the C.L.R.I. could benefit the Bombay State was discussed, during this visit, with the members of the Indian Leather Technologists Association, Western Region and the officials connected with the Leather Industry in Bombay State.

TECHNICAL SEMINAR

Livestock and Prospects for Leather Industry in the Phillipines*

BY

THEOPHILA A. VARSOVIA

Philippines is a heavily mountainous and thickly forested country with rich mineral deposits, fine landscapes and volcanoes. It consists of 7109 islands with total land area of 114,830 sq. miles. The Filipinos are mainly a meat-eating nation and so they take better care of their livestock, that is, they are livestock-minded. Livestock farming is of two kinds: one on grass lands and pastures and the other hand-fed, that is in residences. The livestock population figures as reported at 1948 are: Buffaloes 1,964,443; cattle 501,131; horses 146,661; pigs 3,000,000. Figures of population of goat and sheep are not available. Attempts are being made to increase the goat population in the country. The buffaloes, carabaos as the Filipinos call them, are reared for their milk and also for draught purposes. The cattle are useful so far as their beef and milk are concerned. However, slaughter of buffaloes is now being progressively banned. Eating dead animals also is prohibited. The Government is now concentrating on making the country self-sufficient with respect to beef and milk for during the last War there was wanton destruction of animals. Pigs and chicken are being reared in larger numbers. There is also a programme for improvement of livestock. Rinder pest has

*Condensed from the talk given on 13-6-1958. Mrs. T. A. Varsovia, Veterinary Doctor from Philippines has been deputed by the Philippines Government for training in Leather Technology, at the Central Leather Institute, under the Colombo Plan.

been completely eradicated and fortunately warble is unknown in the country. The livestock are given balanced diet containing all necessary ingredients. The Government has also a utilisation service which is concerned with maintenance of national slaughter houses, tanneries and plans for processing condemned carcasses and the by-products. The animals are slaughtered in this national slaughter houses, flayed and then put in cold storage.

Pre-War figures only are available relating to slaughter of animals: Buffaloes 73,807; cattle 109,650; horses 5,680; goat 59,582; sheep 18,314. The skins are not utilised either for export or locally. Actually all the goat and sheep skins are wasted by burning. The hides produced are partly consumed locally and the rest exported. As regards the quality of hides it is better than that of Indian and worse than that of Burma. As regards defects in hides, branding which was once widely prevalent, is now being slowly eradicated by restrictive legislation. It is recommended to brand if at all necessary, only on the fore-legs and such other portions not valuable for leather making. Mechanical damage due to barbed wire also is common. The average weights of the hides and skins are as follows: Buffalo hide 30-35 kg; cattle hide 20-25 kg; horse hides 18-20 kg; goat skin 4-5 kg; sheep skin 4-5 kg.

The raw materials, i.e., hides are the most expensive item in preparation of leather. Marine salt is available in plenty in the country. Lime prepared from lime stone is available. However, shells also are available and shell lime can be prepared. Acids and alkalies are being manufactured in the country in the post-war period. There are rich chromite deposits in the country and so the prospects for chrome tanning are quite bright if the material could be further processed. The country has available a number of vegetable tanning materials; (1) Mangrove — *Rhizophore conjugata*, (2) *Pithecolobium dulce* — Kamachili, (3) *Terminalia*

edulis, (4) *Calophyllum inophyllum*, (5) *Albizia lebbek-vides*, (6) *Areca catechu*, (7) *Sonneratia pagatpat*, (8) *Xylocarpus abovatoz*, (9) *Ceriops tangal* and (10) *Bru-guiera parviflora*. Of these the first one is mainly exported and the second utilised by the local industry. However, the bad odour associated with this material is a chief draw-back. Other materials like colophony and casein are available in the country. However, casein is not produced in large quantities.

The main kinds of leathers manufactured in the country are sole leather tanned with *Pithecolobium dulce* and chrome leather. There are about nine tanneries located in in a single town making sole leather and one tannery preparing chrome leather. Upper leather, glazed kid, sole and harness leathers are imported from other countries. There is a good market for leather in the country. Non-availability of skilled labour is one of the problems. However, given the necessary facilities and training, the Filipino would be able to prepare as good leather, if not better, as manufactured in other countries. The country has expert shoe makers.

Since the bad odour associated with use of *pithecolobium dulce* in manufacture of leather can be removed by blending with myrobalan, steps will have to be taken to import this material from India to the country, so as to utilise fully the indigenous tanning material which is otherwise good. The leather industry is not new in the country. It has been neglected and undeveloped. So the Government should give top priority for development of the leather industry. Obtaining technical help from abroad might be necessary in this development. Preventing the colossal wastage of goat and sheep skins through burning animals for food, would result in making available valuable raw materials for the production of glazed kids, lining and chamois leathers.

TECHNICAL SEMINAR

Studies on Shrinkage Phenomenon Formaldehyde Combination Tannage*

BY

K. S. JAYARAMAN

Based on the shrinkage temperature data certain interpretations were made earlier in regard to the mechanism of formaldehyde combination retannages. Some quantitative data have now been obtained in regard to the fixation of formaldehyde in the combination tannages and these data confirm the previous findings and postulates. Full details of this paper will be published in this Bulletin at a later date.

*Summary of the talk delivered on 20-6-1958.

TECHNICAL SEMINAR

Wattle Plantations of South India*

BY

V. S. KRISHNASWAMY

Chief Conservator of Forests, Madras

Madras has been having a flourishing leather trade mainly due to easy availability of vegetable tanning agents in the State. However with increasing demand for Indian leather, the Madras tanners had to get tan barks from other states and also import from other countries especially from Africa. These imports which were 200 tons in 1922-23 reached upto 40,000 tons prior to 1947. The imported tan barks are mainly wattle bark the percentage of tannin in which was found to be very high and the quality uniform. However, the Second World War and the strained trade relations with South Africa, the chief exporting country, soon created the necessity for growing the wattle acacias on a large scale in this country.

The wattles were first introduced in the Nilgiris as early as 1832. However, they were cultivated mainly to supply fuel to the army and also as a nurse crop in tea and cinchona plantations and also as fire and wind belts. It was only in 1939 that efforts were directed at planting these acacias in a systematic and scientific manner for exploitation of their tan bark. The following four wattle species were introduced in the Nilgiris: (1) *Acacia dealbata* (Silver wattle), (2) *Acacia decurrens* (Green wattle), (3) *Acacia melanoxylon* and (4) *Acacia mollissima* or well-known black wattle of commerce.

*Condensed from the talk given on 27-6-1958.

The first one is generally used as adulterant to the green wattle. Though the green wattle was originally valued for its higher tannin content and frost resistance, large-scale planting of *Acacia decurrens* was soon given up in favour of *Acacia mollissima*. *Acacia mollissima* contains a fairly high percentage of tannin and the wood besides being a good fuel, yields short fibred pulp suitable for paper and cellulose industries and for dissolving pulp for rayon industry.

In view of these various uses of wattle, plantations have been now raised on large scale in the State. Upto 1956, 2,662 acres in the Nilgiris and about 4533 acres in the upper Palnis were planted with wattle. Since then as part of the programme for the Second Five Year Plan, a large-scale planting has been taken up by the Madras Forest Department. Plantations have now been carried out even in Coimbatore and Salem districts. At the present rate of raising plantation of 4,700 acres per year, it is expected that after 1965, the Forest Department will have about 45,600 acres under wattle. As the plantations mature, they will be felled on a 10-years rotation at the outside. An acre plantation yields about 20 tons of air dry wood, and 4 to 5 tons of bark. From 1968 onwards about 4,200 acres of the plantations may become ready for exploitation to yield about 19,000 tons of wattle bark and 84,000 tons of wattle wood (the cost of raising an acre of wattle plantation is Rs. 36.50 in Nilgiris and Rs. 62.75 in the upper Palnis; the difference is due to high labour cost and difference in plantation techniques).

The wattle tree is found to thrive well between elevations of 5,500 feet and 7,500 feet in the Nilgiris and between 6,000 feet and 8,000 feet in the Palni Hills. The mean maximum and minimum temperatures in the shade are 57°F and 35°F respectively. Rain fall varies between 50 to 80" with over 100 rainy days in a year. The tree does not grow

well in areas of higher rain fall. It comes up well in grass lands and abandoned cultivated lands, excepting swamps.

Planting Techniques. The seeds are pre-treated by soaking in boiling water. By this they become viable to the extent of 53 to 60 per cent. The wattle seedlings are raised in nurseries, which are sown by 15th October at the latest, of the year previous to the year of planting. When the seedlings reach a height of 4 to 6", they are pricked out and mossed and kept well protected against excessive sun and drip till the planting season. In the meanwhile, pits are dug and area scraped free of all vegetation. The soil is enriched with N.P.K. fertiliser. Planting commences from May and is completed by June or July. As wattle is intolerant of root competition, periodical weedings are necessary.

The rate of growth of *Acacia mollissima* is rather slow in the first year especially if the seedlings have been raised by direct sowings. Thereafter the growth is fast upto the fifth year and then it gradually declines. The maximum height reached varies from 70' to 50' depending upon the quality. The yield of dry bark attains the maximum value in the eighth year.

The bark samples collected from plantations of various ages have been analysed at the Institute of Leather Technology, Washermanpet. Percentages as high as 49.53 (with *Acacia decurrens*) and as low as 29.43 (with *Acacia mollissima*) have been reported. The results vary from year to year presumably due to variations in the time of collection and quality of the plantation and soil. Also since only small quantities have been collected and supplied, the variation may be due to the genetical differences between trees yielding the bark. However, the high percentages obtained are of significance in that by suitable cross-breeding, it may be possible to evolve strains which give consistently such high tannin content.

Wattle suffers badly in its tender stages from frost. This tree does not suffer from any pest or disease, excepting gummosis, even which does not seem to have an ill-effect. Fire protection operations are of extreme importance as the tree is fire tender.

Problems to be tackled. (1) Against the anticipated demand of about 35,000 tons of wattle bark, Madras will be able to produce only about half this quantity. Due to the specific requirement of soil elevation and rain fall its cultivation could not be extended further than what has been done, in the reserve forests of the State. Attempts to grow them in Assam have proved unsuccessful. The possibility of raising this species in Uttar Pradesh, Punjab and Himachal Pradesh, has been suggested by the Director, Central Leather Research Institute, to Government of India.

(2) Considerable hybridisation occurs especially between *Acacia dealbata* and *Acacia mollissima*, as these flower at about the same time. Consequently, the yield of tannin is affected. Even amongst trees of one species the tannin content varies from tree to tree and so it may be desirable to evolve strains yielding the highest tannin content. Wattle grows at high elevations and babul on plains. So if hybrid of these two could be evolved, it would be then possible to grow hybrid species in the plains so that larger cultivation would be possible. This needs a geneticist. It is proposed to tackle this problem at the Forest Research Institute, Dehra Dun.

(3) Methods for collecting, handling, grading, and storage of locally available barks could be standardised so that the quality is comparable to that of the imported material.

(4) Information so far collected on the species grown in India is scanty. The variation of tannin content with thickness, season, age, etc., are studies, which could be taken up in collaboration with the Central Leather Research

Institute. If the age at which the tannin content of the bark attains its maximum value is determined, then a rotation could be fixed up to give maximum yield and financial return.

(5) A number of silvicultural experiments could be taken up and it is proposed to start them as early as possible in collaboration with Forest Research Institute, Dehra Dun.

Apart from these problems, attempts must be made to utilise the by-products, as has been done in other countries. The spent bark and wood could be utilised in preparing paper and straw boards. Distillation of the wood yields products as good as those from oak wood. The ash of spent bark could be used as manure. The wattle flowers could be used to produce mimosa perfume.

CLASSIFIED ABSTRACTS

VEGETABLE TANNING

INDIGENOUS TANNING MATERIALS OF EAST PAKISTAN, III. EFFECT OF SONARI UPON GORAN TANNAGE. M. A. Khalique and Mofizud Din Ahmed (Dacca Univ.) *Pakistan J. Sci. Research* **9**, 72-4 (1957); *Chem. Abst.* **52**, 6825 (1958). Goran bark (*Cerriops roxburgiana*) produces an excellent leather but of red colour. Sonari bark (*Cassia fistula*) produces a light colored leather but of lower fixation and diffusion characteristics than goran. Blending produces good leather but very little reduction of color.

PROCESSES AFTER TANNING

MINERAL PIGMENTS FOR COLORING OF LEATHER. A. L. Zaides and R. B. Metlitskaya. *Zhur. Priklad. Khim*, **30**, 1633-41 (1957); *Chem. Abst.* **52**, 5865 (1958). Chemical and x-ray analyses of Fe_2O_3 , PbCrO_4 , and TiO_2 pigments of different origins failed to reveal any structural differences to account for their different properties in leather coloring. Electron-microscopic and x-ray diffraction patterns suggested that the controlling factors were the shape of the particles and homogeneity of size distribution.

APPLICATION OF ACRYLIC COATINGS ON LEATHER. Yu. Ya. Margulis. *Vsesoyuzh. Nauch. Inzh-Tekh. Obshchestvo Legkoi Prom., Materialy Soveshchaniy po Krasheniyu i Otdelke Kozh dlya Verkha Obuvi* **1953** 45-6; *Referat. Zhur. Khim.* **1955**, Abstr. No. 57209. *Chem. Abst.* **52**, 5865 (1958). The effect of additions of alizarin oil, sulfonated fish oil, blood, blood and egg albumin, casein, wax, pigments, and resins on the adhesion strength and the quality of the film are discussed; also the effects of preliminary defatting, surface washing, priming with "emulsion A", and of the leather moisture content before dyeing on the adhesion. Further work is recommended on decreasing the thermoplasticity and thickness of the acrylic coatings and increasing their air and H_2O vapor permeability.

TESTING

REPORT OF WARING BLENDOR SUB-COMMITTEE: PREPARATION OF SOLID EXTRACTS FOR ANALYSIS. J. F. Wagoner, C. A. Blair, E. Facer, F. Luvisi, and R. L. Young, Jr., *J.A.L.C.A.*, **53**, 272 (1958). An interlaboratory experiment has shown that the proposed Waring Blendor technique for the preparation of solid extracts for analysis can be substituted for the present Official Method without significant influence upon the analytical values secured for the tannin analyses of the extracts. However, the statistically designed experiment by which this comparison was made has also yielded the additional information that the precision of the methods of analysis is not so good as is indicated in the present descriptions of the methods.

It is the Sub-committee's recommendation that the Tannin Analysis Committee adopt the Waring Blendor with the screen attachment as the Official Method for the preparation of solid extracts; further, that the Committee should consider experiments to find the causes of the low precision, and that particular attention be given to experiments to determine the between day sources of variation in the analyses.

AN IMPACT TEST FOR LEATHER BASED ON AN ALTERNATING PUNCHING FORCE. Thomas J. Carter, *J.A.L.C.A.*, **53**, 250 (1958). An impact test based on the application of a punching force has been developed to evaluate shoe upper leather. A device delivers repeated thrusts to both sides of a specimen until failure occurs. The number of impacts required to produce cracking of the grain and puncture of the leather increases with increase in diameter of the plunger. The load per unit thickness of leather is inversely related to the number of impacts required to produce failure. Examination of the data obtained with the impact tester indicates that resistance to grain cracking, elongation, and puncture can be satisfactorily evaluated.

The usefulness of the machine has been investigated by determining the effects of lubricants, tannage, and accelerated aging. Straight chrome-tanned leather containing stuffing grease showed higher resistance to puncture on impacting than the similarly tanned leather containing fatliquor. When both leathers are degreased, their strengths are practically equal. This would suggest that the impact test can also be used to evaluate lubricants in shoe leather. Straight chrome-tanned leather showed much greater

resistance to repeated impacting than either chrome syntan (Orotan)-retanned or chrome vegetable-retanned. The results obtained for the various tannages and for accelerated aging were found to be similar to those obtained in other fatigue tests.

THEORIES

THE QUESTION OF THE EXISTENCE OF RETICULIN IN ANIMAL SKIN: A CRITICAL SURVEY OF RECENT LITERATURE. A. Kuntzel, *J.A.L.C.A.*, **53**, 259 (1958). In the corium region of the skin there are two types of connective tissue—collagen and elastin—the difference being mainly histochemical. A third type of connective tissue, 'reticulin', does not exist. Those parts of the skin which have been defined as 'reticular tissues' are in fact collagen of a variant morphology. The introduction of the words 'reticulin' or 'reticular tissue' into the description of the connective tissue of the skin has recently given rise to considerable confusion—reticulin being mistaken for elastin or for soluble collagen (procollagen). The object of this paper is to clear up and correct these mistakes.

THE UNI- AND MULTI-POINT BINDING OF CATIONIC SULFATO-CHROMIUM COMPLEXES BY COLLAGEN—K. H. Gustavson (*Garverinaringens Forskningsinst., Stockholm*). *Arkiv Kemi* **11**, 423-30 (1957) (*in English*); *Chem. Abst.* **52**, 6825 (1958). The mode of reaction of solutions of basic Cr sulfate with collagen (hide powder) has been investigated. Two types of basic Cr sulfates ($\text{Cr}(\text{OH})\text{SO}_4$ with and without Na_2SO_4) were used for the series. Both contained practically all the Cr in the form of cationic complexes. The method is based on ascertaining the distribution of the sulfate groups present in the Cr-collagen compound formed. The sulfate groups exist in 3 forms (1) as sulfato groups in the Cr complex; (2) as protein-bound sulfate; and (3) as counter-ion to the charged Cr. complex unipointly attached to collagen. The different protolysis rates have been estimated by equilibrating the systems at pH 5 and 8. The unipoint reaction is dominant, accounting for about 90% of the number of COOH groups of collagen taking part in the Cr fixation. Only about 10% of these groups are able to combine with the bivalent sulfat-Cr cation by complete discharge of the complex. The latter type of reaction is responsible for the cross-linking and stabilization of the collagen chains, which is effected by relatively small amounts of Cr. The bipoint fixation appears to be favoured in the early

stage of reaction, while the unipoint reaction is dominant in the later stage.

THE REACTION OF VEGETABLE TANNING EXTRACTS WITH CHROMIUM SULPHATE TANNED COLLAGEN. K. H. Gustavson, *J.S.L.T.C.*, **42**, 149 (1958). The paper reaffirms the fact that pretanning of collagen (hide powder) with cationic sulphato-chromium complexes markedly increases the irreversible fixation of vegetable tanning extracts as compared to their fixation by untreated collagen. The degree to which vegetable tannins are fixed by chromed collagen differs widely for the various extracts. Similarly, increasing the amount of fixed chromium in the collagen also affects the uptake of the different extracts. Lightly prechromed hide powder carrying up to 4-5% of Cr_2O_3 fixed by collagen on the basis of the protein, shows much greater relative increases of the additional fixation of vegetable tannin extracts on a Cr_2O_3 basis as a result of the incorporation of cationic chromium complexes with collagen, than do more highly chromed specimens. The present findings do not accord with suggestions that the additional tannin fixation which follows the binding of cationic sulphatochromium complexes by collagen is due entirely to incorporation of the tannins in the chromium complexes and not to increased reactivity of the tannin-binding groups of the collagen.

The results indicate that the sulphato-chromium-collagen compound (chrome leather) reacts with and binds constituents of vegetable tanning materials in at least four different ways, additional to the reaction with protein sites involved in the vegetable tanning of normal unchromed collagen. These involve—(i) Additional basic groups of collagen, made available by rupture of the internal salt-links owing to discharge of the carboxyl ions by the chromium complexes, (ii) Displacement of sulphate groups present as gegenions on the collagen-fixed polyvalent chromium complexes, (iii) Displacement of sulphato groups in the chrome complex, (iv) Straight co-ordination of the tannins on the chromium atoms, replacing aquo groups.

The greater binding of vegetable tannins by low-chromed specimens, relative to Cr_2O_3 fixed, may be due to the fact that the main activation of the basic protein groups is achieved even by the binding of small amounts of chromium. Further, if secondary formation of non-cationic chromium complexes occurs during the prolonged periods of tanning required to obtain high chromium

content, this would impair the tannin fixation because of interference with the basic and non-ionic groups of collagen. The effect of ionic sulphate groups in the chromed collagen on tannin fixation and on the stability of the fixed chromium is accentuated.

With regard to the partial displacement of sulphato groups which frequently occurs in vegetable retanning, about half of these groups (one equivalent SO_4 per two atoms of Cr) are easily displaced, while the other half appear to be firmly bound, possibly due to their functioning as $-\text{SO}_4-$ bridges between two atoms of chromium.

BYE-PRODUCTS

LEATHERBOARD AND ITS USE IN THE SHOE INDUSTRY—A. J. M. Draper (*Avalon Leatherboard Co., Ltd., Street, Somerset, Engl.*) *Brit. Paper and Board Makers' Assoc., Proc. Tech. Sect.* **38**, 133-44, discussion 145-7 (1957); *Chem. Abst.*, **62**, 5865 (1958)—An account is given of the various types of leather boards and the materials (cellulose fibres, leather, and rubber) used in their manufacture. The various methods of shoe construction are described and the part played by leather board in shoe construction is discussed. Some methods used in testing leather board are given.

THE REACTIVITY OF KERATIN, J. B. Speakman, *J.S.L.T.C.*, **42**, 135 (1958). The newer man-made fibres have transformed the consumer's conception of what is to be expected of textile materials as regards serviceability. Just as leather is meeting increasingly severe competition from synthetic products, so wool is now meeting a severe challenge from an expanding range of man-made fibres in the field of 'easy-care' fabrics, and the challenge cannot be met by reiterating the advantages of wool, great though they are. It must be met by devising methods of modifying the properties of wool to suit particular needs, e.g., increased resistance to wear, dimensional stability, and speed of drying.

Early successes in such work were based on disulphide bond break-down, but chief attention is now being paid to cross-linking and polymerisation reactions. As regards the former, progress is handicapped by lack of precise knowledge of the differences in composition between the crystalline and amorphous phases of keratin, but it has been shown that very frequent cross-linking is

essential if the amorphous phase is to be reinforced to a commercially useful extent. The amorphous phase can, however, be reinforced easily by preferential internal polymerisation of vinyl compounds, for which three general methods have been developed. Even greater success comes from the use of monomers which combine with reactive side-chains in the keratin and lead to the formation of graft co-polymers. Reactions of this kind should give new methods of increasing the resistance of wool to shrinkage, wear, chemical attack and microbiological attack, and the ability to confront an expanding range of man-made fibres with equanimity.

PATENTS

GLUTARIC ACID MIXTURES FOR THE ADJUSTMENT OF THE ACIDITY OF POWDERED SYNTHETIC TANNING AGENTS—*Farbenfabriken Byer A.-G. Brit.*, 785, 104, Oct. 23, 1957; *Chem. Abst.*, 52, 5866 (1958). The acid mixture obtained as a by-product in the oxidation of cyclohexane, cyclohexanol, cyclohexanone, or mixtures thereof, to adipic acid, which mixture consists of glutaric acid 70, succinic acid 10, adipic acid 15, and oxalic acid 5%, is used to adjust the pH of a synthetic tanning agent. This mixture may either be added prior to the drying of the syntan solution, or it may be added to the dried product.

CONDENSATION PRODUCTS OF SULFONES OF MONOHYDRIC PHENOLS, NONAROMATIC AMINES, AND FORMALDEHYDE AS RETANNING AGENTS—*Martin Meister and Gustav Mauthe (to Farbenfabriken Bayer A.-G.) U.S.* 2,809,088, Oct. 8, 1957; *Chem. Abst.* 52, 5866 (1958). Retanning processes which comprise retanning a previously tanned leather with a tanning liquor containing up to 25% of a salt of the condensation product obtained from sulfones of monohydric phenols with non-aromatic monoamines and HCHO at temperatures of about 100° are described. Specific claims are made for the use of bis-(4-hydroxyphenyl) sulfone, bis-(4-hydroxy-3-chlorophenyl) sulfone, and bis [4-(hydroxymethyl) phenyl] sulfone along with morpholine or ethanolamine in the condensation with HCHO. These products serve as cationic tanning agents and yield leather with excellent surface lustre, light colour, and good fullness.

WHITE LEATHER PRODUCED BY PRECIPITATING IN SITU ZINC SULFIDE AND SULFHYDRATE. *Harlen A. Depew and Geo. R. Waitkins (to American Zinc, Lead & Smelting Co.)*

U.S. 2,809,878, Oct. 15, 1957; *Chem. Abst.* 52, 5866 (1958). A process for the tanning of hides is described which consists of the essential steps of impregnation of hides with a water-soluble sulfide followed by impregnation of the hides with a solution of Zn. salt to precipitate sufficient ZnS to tan the hides. An example describes a 1st bath containing 6% NaSH and 6% NaCl while the 2nd bath is composed of 13.2% ZnSO₄·H₂O and 6% NaCl. The hide pieces were impregnated with the 1st bath by a 4-hr. drumming in a ball mill; these impregnated pieces were then drummed in the 2nd bath for 3 hrs. allowed to stand overnight, and again redrummed for 2 hrs. Fat-liquoring with an alum oil emulsion containing 20% alum oil and 12% NaCl during a 1.5-hr. drumming, followed by washing of the fat-liquored leather, produced the final leather which was air-dried. The leather showed an uneven layerwise deposition of Zn salt, varying from 6.6% Zn on the grain side to 2.6% Zn on the interior split. The shrinkage temperature of the layers reflected the Zn content, varying from 82° on the grain side to 62° in the interior.

RECOVERY OF LEATHER SCRAP. *Frederick B. Forward. U.S.* 2,808,398, Oct. 1, 1957; *Chem. Abst.* 52, 5866 (1958). Leather scrap, soaked in water at about 190°F for 2 hrs. forms a rubbery mass devoid of the original leather shape; drying and curing of this mass at about 125°F for 14 hrs. reduced the moisture content to about 8%. The hard, brittle chunks produced can be pulverised to yield leather dust with very little residual fibrous mass. The product can be compounded in finishes designed to give wood or metals with the finish characteristics of real leather.

UREA DERIVATIVES OF PROTEINS FOR GLUE MANUFACTURE. *Harland H. Young and Edward F. Christopher (To Swift & Co.) U.S.* 2,816,099, Dec. 10, 1957; *Chem. Abst.* 52, 5867 (1958). Water-soluble protein isocyanate derivatives can be formed without use of HNCO esters. One mole HNCO is used per mole protein containing free NH₂ group. Water-soluble cyanates as well as derivatives forming HNCO in warm aqueous solution can be used. For example, adjust 500 g. acid-cured gelatin liquor containing 10% solids to pH 6.0-6.8 after warming to 120°F. Add 1 g. KCNO in 9 g. water slowly with stirring. The product retained its gelling power and viscosity, but its isoelectric point was decreased from 8.6 to 5.7. Other raw materials used include bone glue liquor, casein, soyabean protein, cotton seed protein,

peanut protein, fresh ox blood, concentrated tank rendering water (fat-free), and washed, degraded, minced pork skins.

TANNING EXTRACTS — *Produits chimiques Charles Monnet, S.a.r.l. and Raymond A.A. Dru. Fr. 1,028,319*, May 21, 1953, *Chem. Abst.* **52**, 6825 (1958). The small amounts of Fe and Cu salts that contaminate tanning materials are precipitated from their solutions by an alkali metal ferrocyanide in the presence of an alkali or alkaline earth metal sulfide, hydrosulfide, or polysulfide. By this method the necessary amount of the precipitating salt is greatly diminished. For example, to a liquid extract of chestnut wood having a density of 3.5° Be. and the dry residue of which has been determined by treatment at 55-60°, is added 0.1-0.2% (of the dry residue) 20% (NH₄)₂S dissolved in water, and then immediately, 0.08-0.2% crystallised K. ferrocyanide dissolved in water. After mixing, the liquid is cooled to < 20° and the entire Fe and Cu is precipitated on standing.

SYNTHETIC TANNING MATERIALS. *Farbenfabriken Bayer A.-G. (Heinz Schultheis and Detlef Delfs, inventors) Ger. 927,331* May 5, 1955; *Chem. Abst.* **52**, 6826 (1958). Sulfonation at temperature above their melting points of mixtures of aromatic hydrocarbons containing ≥ 2 condensed nuclei, mono- and (or) disulfonic acids, aliphatic aldehydes yielding HCHO upon decomposition or o-chlorosubstituted phenols gives tanning materials (I) of good stability, compatibility with vegetable I, and a good ability to disperse the mucous parts and phlobaphenes in org. I. Thus, 130 g. each of naphthalene and H₂SO₄.H₂O were fused at 160° stirred for 1 hr. and cooled to 95°. A mixture of 64 g. o-chlorophenol (II) and 87.5 g. aqueous 30% HCHO solution was slowly (1 hr.) added, stirred for 1 hr., cooled to 80°, the pH adjusted to 7 with N NaOH, and then to 3.2 with a mixture of 5 g. HCOOH and 25 g. glacial AcOH, to yield a viscous liquid containing 56% I. This produced clear, almost-white, leather (III). Naphthalene, sulfonated in a similar manner, yields I which produces light-colored III. By use of 76 g 6-chloro-m-cresol instead of II as in the 1st example, a somewhat darker III is produced. Phenanthrene (180 g) produces light-gray III, while anthracene produces gray III.

SULFONATED LIGNIN FROM SULFATE WASTE LIQUORS, SUITABLE FOR USE AS TANNING AGENT. *Stiftelsen Svensk Cellulosaforskning (E. Adler and E. K. M. Hagglung, inventors). Swed. 160,770*, Oct. 8, 1957; *Chem. Abst.* **52**,

6826 (1958). Lignin from sulfate waste liquors is treated at an elevated temperature in an alkaline medium with a sulfite in the presence of HCHO. CH₂SO₃H groups are introduced into the aromatic nucleus of the lignin molecule during this reaction. The conversion can be accomplished in 2 stages. First, primarily CH₂OH groups are introduced in the ortho position relative to free phenolic OH groups. Second, CH₂—OH groups in the hydroxymethyl derivatives obtained in the 1st stage are transformed into SO₃H groups. The products, which generally contain about 1 SO₃H group per 5 MeO groups, are soluble in H₂O under neutral or slightly acid conditions. For example, 500 g. black liquor lignin is treated under reflux for 6 hrs. at 90° with 4 l. of an aqueous solution containing 250 g. Na₂SO₃ and 125 g. 40% HCHO. The solution is treated with an H⁺-saturated cation exchanger and is evaporated to dryness if necessary.

TREATING LEATHER PRODUCTS. *S. N. Ramm and A. S. Turbin U.S.S.R. 108,264*, Oct. 25, 1957; *Chem. Abst.* **52**, 6826 (1958). Leather products are rendered hydrophobic by treatment with a solution of dispersion of a synthetic high polymer, e.g. polyisobutylene, in a solid hydrocarbon solvent, such as high-melting paraffin.

GLUE. *M. Pikarsky, Israeli 10,317*, Dec. 5, 1957; *Chem. Abst.* **52**, 6826 (1958). Pure, light-colored, high-quality glue is extracted from a material obtained by repeated treatment of crushed green or previously degreased bones with 1-10% aqueous H₃PO₄ for 6-24 hrs., followed by removal of residual acid by washing with H₂O. Precipitation of residual phosphates from the glue solution as insoluble Ca salts and subsequent filtration and decantation result in a low ash content. H₃PO₄ and its salts are recovered as CaHPO₄ or other phosphate salts. Experiments showed an increase of yield of 8-10% over the glue production by conventional methods.

NOTES & NEWS

FOREIGN MARKETS FOR LEATHER GOODS

Efforts to find foreign markets for consumer goods made by small scale industries in India are steadily yielding results.

As part of the general export promotion drive, the National Small Industries Corporation, set up by the Government of India to provide marketing and other assistance to small industries, has been exploring foreign markets for such products as leather, foot-wear, woollen and cotton hosiery, sports goods, coir products, builders' hardwares and engineering goods.

A large order for 2.5 lakhs pairs of shoes from the Soviet Union has already been executed by the Corporation through a number of small manufacturers who got for the first time an opportunity to send out their products to distant countries.

Another order for 65,000 pairs of ladies' shoes has been received from the Soviet Union. This order is under execution and is expected to be completed shortly. An order for 54,000 pairs of men's ladies' and children's shoes from Poland has also been executed in part.

— *The Hindu*, dated 7-7-58.

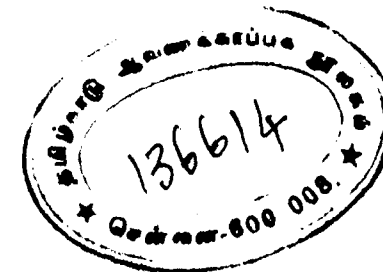
C. L. R. I. NEWS

Dr. Y. Nayudamma has been nominated to serve as a member of the Panel set up by the Ministry of Commerce and Industry, Government of India, for drawing up a programme for the development of leather and leather goods industry.

Mr. P. S. Venkatachalam, Junior Scientific Officer, has returned after completion of his period of deputation to U.K., under the Colombo Plan.

VISITORS

Name	Date of Visit
K. P. Gopalan, Minister for Industries, Kerala State	.. 23-6-1958
P. V. Nair, Director of Industries and Commerce, Kerala State	
K. K. Rajah, Deputy Director of Industries, Kerala State	
S. N. Mushnan, Deputy Minister for Agriculture, Madhya Pradesh	.. 10-7-1958



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சே. எண் :

ப. எண் :

வழங்கிய நாள். (1)	திரும்பிய நாள். (2)	வழங்கிய நாள். (1)	திரும்பிய நாள். (2)

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