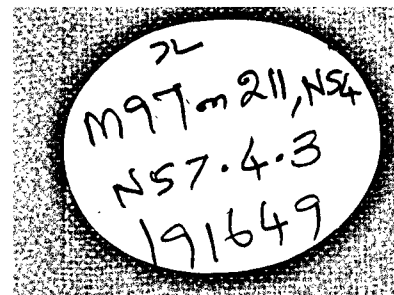


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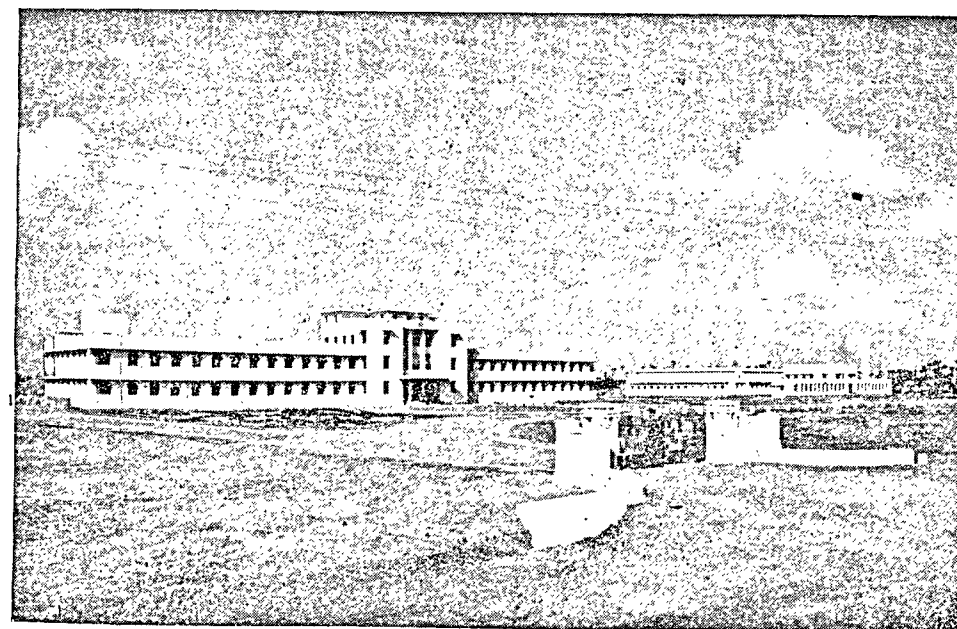
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The Central Leather
Research Institute
Madras



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COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH
INDIA

Bulletin of The Central Leather Research Institute

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October, 1957

No. 3

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We regret very much for the delay in the publication
of this issue.

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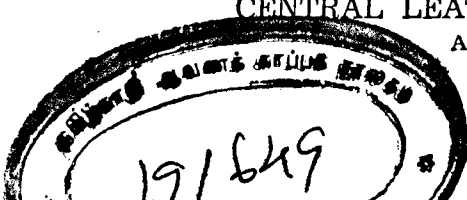
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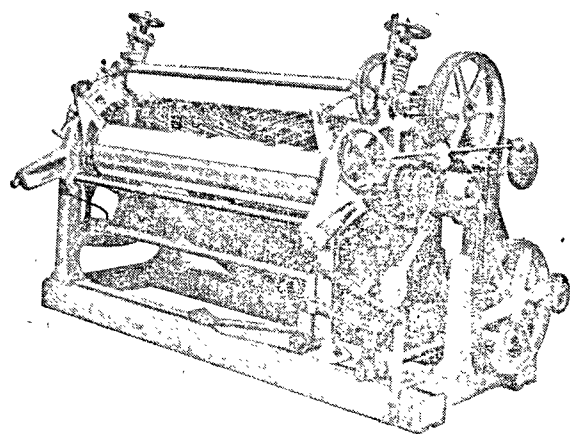
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SURVEY OF THE INDIGENOUS TANNING MATERIALS OF THE MADRAS STATE—PART IV *

Dhawa Leaves (*Anogeissus latifolia*)

J. B. RAO & Y. NAYUDAMMA

SUMMARY

The utilization 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, blends 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.

The leaves of Dhawa as a tanning material has been known since a long time and the material has been used for mordanting and bleaching of leathers and for the manufacture of certain types of leathers by village tanners using it in admixture with other tanning materials.¹ Very little is known in regard to its use in E.I. tanning industry which is the largest unit in Indian vegetable tanning industry. Such a study has now been made. The material by itself has not been found to be useful in E.I. tanning as it imparts a very objectionable greenish tinge to the leather tanned with it. But when used in blends, it has the unique advantage of reducing the objectionable red colour produced by certain indigenous tanning materials like Goran and Karada which are available in plenty but are not popular with the trade. Thus by blending these materials, the individual defects of Dhawa, Karada or Goran are overcome and leathers of good quality comparable to those produced by tanning with imported wattle bark are produced.

* Presented at the Seminar held on 20-5-'57.

The tender leaves contain a high percentage of tannins, nearly 20 to 30 per cent, whereas the mature variety contains 12 to 20 per cent tannins. A systematic study of the mature variety and a complete chemical analysis and practical tanning tests have been made and the results are reported in this paper.

The popular names of the leaves are

Dhawa	— Hindi.
Dinduga	— Kanarese.
Vellaynaga	— Tamil.
Chiriman	— Telugu.

The tree is distributed throughout the sub-Himalayan tract and on the hills of Southern India.

Though the exact availability of the leaves in the various forests is not known, it is presumed that in view of its wide distribution, the leaves are available in plenty for use in the tanning industry.

The leaves obtained from Madurai East division were first analysed for chemical characteristics like tannins, non-tannins, acids, salts, sugars, etc., and the results are recorded in Table I.

TABLE I

Tannins	..	18%
Non-tannins	..	16%
Moisture	..	10.6%
Insolubles	..	55.4%
Tannin/Non-tannin Ratio	..	1:10
Total acids	..	69 m.gm. eq. per 100 gms. T. Sols. Titration to pH 6.5 with N/20.
Total salts	..	160 m.gm. eq. per 100 gms. of T. Sols.
Acid/Salt Ratio	..	0:43
Sugar as d-Glucose	..	1.02%
Ash	..	5.20%
Weak acids	..	66 m. gm. eq. per 100 gms. of T. Sols.
Salts of weak acids	..	150 m.gm. eq. per 100 gms. of T. Sols.
Colour ½% sol./1 cm. cell	..	Y 10.5 R 6.0
pH of analytical solution	..	4.7

The results of acids and salts of the Sicilian sumach and Indian Dhawa leaves as reported by Burton² along with our results for Dhawa leaves obtained are given in Table II.

TABLE II

Tanning Material	Worker	Acids	Salts
Sicilian Sumach	Gosh reported by Burton	90.0 m.gm. eq. per litre of 100° Bk. liq. or 32 m.gm. eq. per 100 gm. of total sols.	393.0 m.gm. eq. per litre of 100° Bk. liq. or 158 m.gm. eq. per 100 gm. of T. Sols.
Dhawa Leaves	Gosh reported by Burton	149 m.gm. eq. per litre of 100° Bk. liquor or 60 m.gm. eq. per 100 gm. of T. Sols.	486 m.gm. eq. per litre of 100° Bk. liquor or 192 m.gm. eq. per 100 gm. of T. Sols.
Dhawa Leaves	Our results	69.0 m.gm. eq. per 100 gm. of T. Sols.	160 m.gm. eq. per 100 gm. of T. Sols.

(i) Blend of Karada and Dhawa

The tannins of the Dhawa leaves are of the pyrogallol type. But unlike myrobalans and divi-divi, which are also of the pyrogallol class, the amount of acids in Dhawa leaves is not so high and is a distinct feature of the Dhawa leaves. The characteristic properties of pyrogallol type of tannins containing high amount of acids impeding the penetration of tannin and thus making them unsuitable for tanning purposes by themselves are not present in case of Dhawa leaves. Dhawa leaves have been used with success for tanning certain class of light leathers for book-binding purposes, etc. The moderate acidity and high salt content are perhaps also responsible for another unique property of the leaves, namely the leathers tanned with the leaves are very fast to light. Sicilian sumach is reported to be less sensitive to light as compared to Indian Dhawa. This is attributed to the difference in the nature of acids present. Burton² reported that, in Indian sumach, a large proportion

of the acids are present as tannin acids, whereas in Sicilian sumach, a large proportion of the acids present are non-tannin acids. Burton² further confirmed the observation

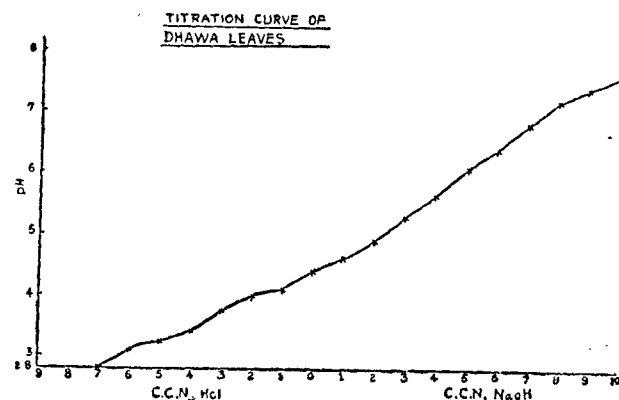


Fig. 1.

of Sourlanges and Atkin³ that the Sicilian sumach tannin was uncarboxylated. But in the Indian variety, the presence of large amounts of tannin acids may be indicative of the presence of a free carboxyl group and as such its constitution may be entirely different from the Sicilian variety. Further work may be necessary to confirm the same. The potentiometric titration studies of the Indian Dhawa leaves have been made and the titration curve of the same is shown in Fig. 1. It is, however, observed from the titration curve that most of the salts and acids present in Dhawa leaves are present as weak acids and salts of weak acids.

Preparation of tannin extracts: The T/NT ratio is not very high in the leaves and as such may not be useful for the preparation of extract. All the same, an extract has been prepared out of the leaves and it was found to contain only 38.5% of tannins which is rather low and not advantageous from the extract point of view. Leaching experiments have been conducted with the leaves and it has been found that 85% of the tannins in the leaves are leached out at the end of the 6th day. The leach liquors have been

concentrated and dried in vacuum and the extract has been analysed for its tanning content. The results are given in Table III.

TABLE III
Analysis of the Dhawa Extract

		%
Tannins	..	38.5
Non-tannins	..	47.5
Moisture	..	9.5
Insols.	..	4.5
Colour ($\frac{1}{2}$ % sol./1 cm. cell)		
Y	..	8.5
R	..	4.5
pH of analytical sol.	..	4.15

Tanning trials: Preliminary tanning experiments with Dhawa leaves alone have not been very encouraging from the point of view of the use in E.I. tanning industry. The traditional method of E.I. tannage was followed in the various tanning trials. Wet salted cow hides were soaked, limed and delimed in the usual way. The pelt was tanned by the traditional method by placing it in between layers of the tanning leaves, and the material tanned according to the two pit system for 18 days. An amount of leaves equivalent to the expected yield of the leather (on the basis of 16% tannin on the weight of the pelt) was used for tanning.

The leathers though having good feel and substance, had a very slight greenish tinge, which may not be acceptable to the E.I. tanner. The leathers were analysed chemically and the degree of tannage was quite high. Except for the colour, all other physical and chemical characteristics were satisfactory (Table IV).

Having found that the leaves themselves are not quite suitable for E.I. tanning and keeping in view the bleaching

properties of the material, preliminary experiments have been conducted by blending the leaves with materials like Goran and Karada (which normally give dark coloured leathers and as such unsuitable for E.I. tanning purposes) with a view to see if the dark colour produced by these materials could be improved so as to be useful in E.I. tanning industry. The results have been found to be very satisfactory. The leathers produced by the blends of (1) Goran and Dhawa, (2) Karada and Dhawa, (3) Konnam and Dhawa have all been found to have good colour and feel acceptable to the E.I. tanning industry. A proportion of 1 : 1 of the leaves and barks respectively calculated on their tannin contents have been found to yield the best results. The preliminary experiments having been found satisfactory, large scale tanning trials with the blends of:

TABLE IV
Analysis of Leathers tanned with Dhawa leaves

Hide Substance	..	40.90%
Insoluble ash	..	0.87%
Water solubles	..	6.24%
Total ash	..	1.30%
Oils and Fats	..	5.71%
Fixed Tans	..	31.10%
Degree of tannage	..	76.00

(1) Goran and Dhawa, (2) Karada & Dhawa, (3) Konnam and Dhawa have been carried out in the tannery. The traditional method of E.I. tanning process was followed with parallel experiments conducted with wattle bark for comparison. The physical, chemical and microscopical properties of the leathers are given in Tables V, VI and VII respectively.

Thus the physical characteristics of the leathers tanned with the blend of Karada and Dhawa are comparable with those of wattle.

TABLE V
Physical Characteristics

	Genl. appear- ance	Colour	Feel	Fullness	Cracki- ness	Tear strength	Tightness of grain	Yield
	1	2	3	4	5	6	7	8
Expt.	Good	Lighter, equal to E. I. tanned leather.	Somewhat firm.	Full.	No	Strong.	Tight.	44
Control	Good	Slightly reddish.	Firm.	Full.	No	Strong.	Tight.	42

TABLE VI
Chemical Characteristics

	Expt. %	Wattle (Control) %
Hide Substance	.. 42.70	41.2
Fats & Oils	.. 5.40	6.1
Moisture	.. 12.20	12.0
Ash content	.. 0.45	0.5
Water solubles	.. 8.08	8.4
Ash of water solubles	.. 0.35	0.3
Ash of Insols.	.. 0.10	0.2
Fixed Tannins	.. 31.52	31.6
Degree of tannage	.. 73.80	76.6
pH of water Sols.	.. 4.10	4.2

The chemical characteristics of the leathers tanned with the blend of Dhawa and Karada compare very closely with those of wattle tanned.

It is seen that the blend of Dhawa and Karada gives a leather of light colour equal to that of E.I. tanned leather. The leather is soft, feel and general appearance good. The addition of Dhawa to Karada and Goran barks appears to have mellowing action and the resultant leathers are extremely good in quality comparing in physical, chemical and microscopical qualities with those of wattle.

TABLE VII
Microscopical appearance

Karada and Dhawa ..	Ill defined, slightly thin and very disordered fibre bundles, showing slightly loose weave and less than medium angle. A little more than medium amount of splitting.
Wattle ..	Fairly bold, fairly full, slightly disordered fibre bundles showing loose weave and less than medium angle. Very large amount of splitting.

(ii) *Blend of Dhawa and Goran*

Large scale tanning experiments with this blend of Dhawa and Goran in equal proportions, have been carried out. The traditional method of E.I. tanning was adopted. The physical, chemical and microscopic characteristics of the leathers tanned with the blend and wattle control are detailed in Tables VIII, IX and X respectively.

TABLE VIII
Physical Characteristics

	Gen. Appearance	Colour	Feel	Fullness	Crackiness.	Tear strength	Yield
Expt.	Good.	Light	Firm	Full	No	Strong	40
Wattle	Good.	Light, but pinkish.	Firmer	Full	No	Strong	42

TABLE IX
Chemical characteristics

	Expt. %	Control %
Hide substance ..	45.42	42.59
Moisture ..	15.60	15.60
Fats & Oils ..	7.39	6.74
Ash content ..	0.50	0.46
Water soluble matter ..	6.21	4.68
Ash of Insols. ..	0.04	0.03
Fixed Tans ..	25.39	30.36
Degree of tannage ..	55.84	71.29

The degree of tannage of the leathers tanned with the blend is lower than that of wattle, but this could be easily overcome either by prolonging the period of tannage or addition of organic acids. Though the degree of tannage is lower than that of wattle, in view of the other characteristics such as general appearance, colour, feel and other physical characteristics being comparable with the wattle tanned leathers, the blend may be safely used in E.I. tannage. This blend has great potentiality in E.I. tannage as Goran is available in plenty and is at present not being used because of its objectionable colour. Dhawa not only overcomes this defect but also mellows down the very astringent tanning properties of Goran.

TABLE X
Microscopical appearance

Dhawa and Goran ..	Less than fairly bold, slightly thin and disordered fibre bundles, showing fairly compact weave and less than medium angle. More than medium amount of splitting.
Wattle ..	Less than fairly bold, slightly thin and disordered fibre bundles, showing loose weave and less than medium angle. Medium amount of splitting.

There is a close resemblance of microscopical characteristics between the wattle tanned leathers and leathers tanned with the blend.

(iii) *Blend of Konnam and Dhawa :*

Large scale tanning experiments have been conducted with a blend of Dhawa and Konnam in equal proportions and the leathers produced have been extremely good in colour and feel and are better than wattle tanned leathers. The usual process of E.I. tannage was adopted. The physical, chemical and microscopical characteristics of the leathers are given below. This blend can be used both for Kips as well as skins successfully.

TABLE XI
Physical Characteristics

	Gen. Appearance	Colour	Fullness	Smoothness	Tightness	Crackiness	Tear strength	Yield
Expt.	Good.	Very good.	Full	Smooth.	Tight.	No.	Good.	42
Control	Good.	Slightly pinkish.	Full	Smooth.	Tight.	No.	Good.	42

TABLE XII
Chemical Characteristics

	Expt. (Dhawa & Konnam)	Control (Wattle)
Hide substance	.. 44.69	43.00
Fats & Oils	.. 4.71	5.00
Moisture	.. 15.60	15.60
Ash content	.. 0.56	0.50
Water solubles	.. 7.00	7.00
Ash of Insols.	.. 0.10	0.15
Fixed tans	.. 27.40	24.25
Degree of tannage	.. 61.10	68.0
pH of water solubles	.. 4.0	4.2

TABLE XIII

Microscopical Appearance

Dhawa and Konnam ..	Fairly bold and fairly full and fairly ordered fibre bundles, showing fairly compact weave and medium angle, medium amount of splitting with slight resticking.
Wattle ..	Ill defined, slightly thin, and disordered fibre bundles, showing slightly loose weave and low angle, medium amount of splitting with slight resticking.

This blend of Konnam and Dhawa has been found to be most promising. The colour of the leathers has been extremely good as well as feel and other characteristics. This can safely replace the Wattle bark in E.I. tannage.

The leaves have also been used for retanning of chrome tanned leathers and the results were very encouraging. The quality of the leather has been very much improved. The grain, feel and fullness have all been improved considerably.

Extracts of Blends of Goran and Dhawa and Karada and Dhawa which have been found to be suitable for E. I. tanning have been prepared and the tanning content of the extract was much higher than that of Dhawa alone. The colour of the extract was also lighter than the corresponding extracts of Goran and Karada.

TABLE XIV

Analysis of extract of the blend of Dhawa and Goran

Tannins	.. 43.5%
Non-tannins	.. 33.5%
Moisture	.. 14.0%
Insolubles	.. 9.0%
Colour ($\frac{1}{2}$ % tan. sol./1cm. cell)	
Y	.. 10.2
R	.. 5.1

TABLE XV
Analysis of extract of the blend of Karada and Dhawa

Tannins	..	% 46.3
Non-tannins	..	33.9
Moisture	..	12.4
Insolubles	..	7.4
Colour ($\frac{1}{2}$ % tan. sol./1cm. cell)		
Y	..	9.0
R	..	4.9

Conclusions :

Dhawa leaves blended with Goran, Karada and Konnam give leathers of good colour and quality similar to the E.I. tanned leathers and as such, the blends can be used in E.I. tannage as substitutes for Wattle.

The Blend of Dhawa and Konnam can be used for both kip as well as skin tannages.

Though the Dhawa leaves by themselves are not suitable for the preparation of extracts, the blends of it with Goran and Karada, have possibilities of the manufacture of extracts.

Since large quantities of Goran and Karada which are by themselves unsuitable for E.I. tannages are available, Dhawa leaves can be used in conjunction with them successfully for the production of the E.I. tanned leathers.

ACKNOWLEDGMENT

Our thanks are due to the Microscopical laboratory for carrying out the microscopic examination of the leathers and to the forest department, Madras State for the supply of Dhawa leaves.

Chemistry & Physics Division,
20-5-'57

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A NOTE ON THE YELLOW COLOURATION OF CURING SALT IN PRESENCE OF SODIUM SILICOFLUORIDE

SUMMARY

It was observed that when sodium silicofluoride was mixed to increase the bactericidal value of common salt containing Fe salts as impurities, it turns yellowish in colour. The surface of the experimental hide pieces if cured with such salt in admixture with sodium silicofluoride developed yellow colour after some days. Evidences so far obtained are suggestive of the formation of a complex compound, probably of the composition ferrous mono ferri fluoride, FeF_2 , FeF_3 , $7\text{H}_2\text{O}$ which has a distinct yellow colour.

It is well known that sodium chloride alone is not a very efficient curing agent for hides and skins and its bacteriostatic action is for limited period only. So it is of importance to carry out investigations to find out suitable additives which will improve the preservative power of common salt without imparting any harm to the cured hide during the process or to the finished leather. The use of fluorides and silicofluorides were suggested by a number of investigators to have a substantial approach in this direction.¹⁻⁸ But, on the other hand, it has been reported that salt stains cannot be entirely prevented by using fluorides and the finished leather was slightly dull grained and a bit harder.^{9, 10} Dullness of the grain was also observed in the case of sodium silicofluoride.^{10, 11} Rough and preckered edge of the finished leather was also noticed while using sodium silicofluoride.¹⁰ Experimental work on the use of fluorides in curing calf skins by Dempsey and Robertson¹² confirmed the findings of Stuart and Frey¹³ that fluorides are less suitable for use with salt on light skins than on heavy hides. Vogel¹⁴ reported 3-4 per cent lower

pelt yield by the addition of sodium fluoride. So, naturally it is of interest to find out whether the addition of fluorides or silicofluorides to common salt will be really advantageous:

In an experiment in our laboratory to find out the usefulness of sodium silicofluoride hide pieces were cured with common salt having different percentages of sodium silicofluoride. It was observed that the flesh sides of the hide pieces gradually got a yellowish colour after about one week or two. The hide pieces were tested bacteriologically and it was observed that although there was red growth in case of low percentages of sodium silicofluoride, this yellow colour was not due to the presence of bacteria. Further the colour was such as being suggestive of chemical nature. It was also observed that the common salt itself got coloured yellow after a few days when sodium silicofluoride was added to it.

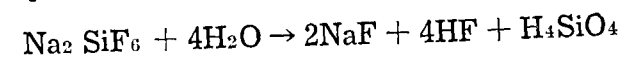
In an attempt to find out the cause for the development of such yellow colour, the salt was tested for the presence of iron salts with KCNS after adding a few drops of HNO_3 . The test was positive. In absence of HNO_3 , however, the specific colour with KCNS did not develop, which indicated the absence of free ferric salts. Usually the presence of ferric salt would induce some colouration to common salt by their presence. As no such colouration was there, it was presumed that ferrous salt which was initially present in common salt, acted in one way or other to develop yellow colour when sodium silicofluoride was added to common salt. Of course the presence of insoluble ferric salts such as oxides and hydroxides in common salt was not excluded by this observation. Different amounts of ferrous salt in the form of ferrous sulphate were added to pure NaCl and this was treated with various amount of sodium silicofluoride and kept under observation. The results obtained are indicated in table below.

TABLE I
Development of yellow colouration in presence of different percentages of sodium silicofluoride

Percentages of Sod. silico-fluoride.	Common salt.	Pure Sodium Chloride	Pure Sod. Chloride and Ferrous sulphate.
0.1	+	—	++
0.3	++	—	++
0.5	++	—	++
0.7	++	—	++
1.0	++	—	++
1.5	++	—	++

To confirm that iron present in common salt is responsible for this yellow colouration, an attempt was taken to extract this yellow material from coloured salt. After trial with a number of solvents it was found that this yellow material could be extracted with amyl alcohol. The amyl alcohol extraction was filtered and then evaporated on water bath when yellow coloured crystals were obtained. These were dissolved in water but the solution was colourless. The solution was tested for iron with KCNS both after addition of HNO_3 and in absence of HNO_3 . The test was positive only when HNO_3 was added. From the above finding it can be assumed that the iron present in the yellow compound may not be in the ferric state. The yellow crystals were also tested for fluoride and the tests were positive.

Now in order to throw some light on the probable mechanism of such reaction the following tentative suggestions are put forward. Sodium silicofluoride in presence of moisture probably undergoes such change.



Of these products HF is an important one and this is expected to have some effect in the production of yellow

colouration in common salt containing sodium silicofluoride. HF in equivalent amount of 1% sodium silicofluoride was taken, diluted with water and added to the curing salt instead of sodium silicofluoride. It was observed that the typical yellow colour appears shortly. It is found from literature¹⁵ that, a complex salt having both iron and fluoride and appearing as yellow crystals as we got in the present case would probably correspond to Ferrous mono-ferri-fluoride, the chemical formula being FeF_2 , FeF_3 , $7\text{H}_2\text{O}$.

Work to elucidate this mechanism further is under progress.

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

Bacteriological Laboratory,
16-3-1957.

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RESEARCH BEARS FRUIT

Practical Demonstration No. 6

Process for the Manufacture of Box Calf

S. N. BOSE

Raw material: Wet salted prime quality calf skins.

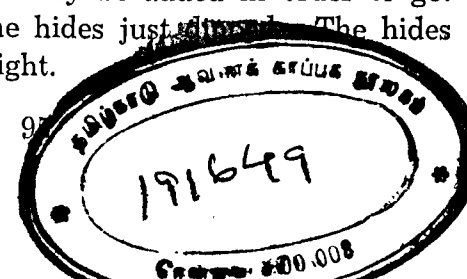
Soaking: The calf skins are soaked in paddle for 4 hours. They are fleshed and again soaked further for one hour in the running paddle and are horsed up for water to drain and weighed.

Liming: Hypo— 2% on soaked weight

Sodium sulphide
(Fused)— $3\frac{1}{2}$ to 4% „ „
Water— 150 to 175% „ „

Hypo is dissolved in a drum containing water. The calf skins are put in the drum and the drum is run for 15 minutes and kept at rest for 45 minutes. Then the drum is run again and one-third quantity of sodium sulphide dissolved in a minimum quantity, say 5 per cent water is added and the drum is run for three minutes (Speed 3 r.p.m.) and kept at rest for 57 minutes.

This process is repeated for the other two instalments. The drum is run for three minutes and kept at rest for 57 minutes after the addition of the third instalment for a period of three to four hours. At the end of the operation, 25 to 50 per cent of water may be added in order to get proper float for keeping the hides just ~~drained~~. The hides are left in the drum overnight.



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Next day, the drum with the goods and liquor is run just as on the previous day for a period of 2 to 3 hours. The hides are then removed, unhaired, and run into a solution of 1½ per cent sodium bicarbonate and 200 per cent water for 30 minutes. Then they are fleshed, scudded and weighed.

Deliming and Bating : The limed pelts are washed in drum in two changes of plain water and delimed with 1 per cent Ammonium sulphate and 150 per cent water on pelt weight for one hour. A fine streak in the innermost layer will show pink colour with phenolphthalein. The hides are then washed and bated with 4 oz. % Pancreol 3 AS and 150 per cent water at 37°C (both taken on pelt weight) maintaining the pH of the bate liquor between 7.4 and 7.6 for 35 to 45 minutes and then the hides are scudded. Then they are weighed and washed in two changes of plain water and horsed up.

Pickling :

Sulphuric acid	..	1¾%	on	bated	pelt	weight.
(66° Be)						
Common salt	..	8½%	„	„	„	„
Water	..	75%	„	„	„	„

15% of the above water is taken in a vessel and the acid is carefully added to it and kept to cool earlier in the morning. 60 per cent water and the salt are taken in the drum and the latter is run to dissolve the salt. The bated pelts are put in this salt solution and the drum is run for 15 to 20 minutes when the acid solution is added in a fine stream over 15 minutes duration and the drum is run for 1 hour and then they are kept immersed in the pickle solution overnight. Next day, the drum is run for 20 to 30 minutes and the pH of the exhaust pickle bath is checked to be 3. At this stage the pickled pelts are horsed up.

Chrome tanning : Chrome extract powder manufactured by the Buckingham and Carnatic Mills, Madras, may be used for chrome tanning. This powder contains 25 per cent Cr₂O₃ and the chrome liquor prepared by dissolving the powder in hot water and left overnight will have a basicity of 33½ per cent and pH 3.3.

5 per cent Bichromate on bated pelt weight equivalent liquor obtained by dissolving 10 per cent chrome extract powder in 10 per cent water on bated pelt weight may be used for tanning.

The chrome liquor is added in three instalments. First instalment of liquor is added to the drum containing 2 per cent salt and 100 per cent water. Pickled goods are put in and the drum is run for 30 minutes and stopped for 30 minutes. The drum with goods is run and the second instalment is added and again run for 45 minutes and stopped for 30 minutes. Afterwards the drum is started and the third instalment is added and the drum is run for 2 hours. Then ¼ per cent Na₂SO₃ dissolved in ten times its weight of water is added in two instalments at an interval of 30 minutes and after the last addition, the drum is further run for 2 hours. Then the goods are left well immersed in liquor overnight. Molasses reduced chrome liquor of 33½ per cent basicity and pH 3.3 may also be used for tanning.

Next day, the drum is run for half to one hour and the tanned hides are horsed up. pH of exhaust tan liquor should be 3.3. The hides are kept in pile for two days and then they are sammed, split, shaved to 1.3 mm. in the butt area and 1.1 in the neck area. Shaved weight is noted.

The shaved leathers are soaked back well, washed in two changes of water and neutralised with ½ per cent Na₂SO₃ and 300 per cent water (on shaved weight) for 15 minutes and then washed in two changes of water and horsed up.

Dyeing and Fat-liquoring :

Nigrosine	..	5 oz %	on shaved weight.
Chlorozol Black E 240	10 oz.%	„ „ „	
Water at 45°C	..	150%	„ „ „

The dyes are mixed together and dissolved in hot water, say 10 per cent on shaved weight at 60°C, strained and kept ready. The above quantity of water is taken in the drum, goods are put in, drum is started and dye solution is fed in and drum is run for 25 to 30 minutes until the dye is absorbed by the leathers.

After dyeing, the dyed leathers are horsed up.

Fat Liquoring :

Cremol F	..	1¼%	on shaved weight.
Neatsfoot oil	..	¼%	„ „ „
Cocconut oil soft soap	..	½%	„ „ „
Water at 60°C	..	150%	„ „ „

Neatsfoot oil and Cremol F are mixed together. Soap is dissolved in hot water. Then, the soap solution is added to the mixture of Cremol F and Neatsfoot oil while stirring the whole thing. This is then emulsified with hot water. In the meantime, the hot water is put in the drum and the leathers are introduced. The fat-liquor emulsion is fed in and drum is run for 30 minutes when ½ per cent Gambier dissolved in hot water and strained already is fed in and drum is run for 10 minutes. Then ⅛% copper sulphate dissolved in cold water is added and drum is run for 10 minutes. Then the leathers are horsed up overnight. In dry climate, the quantity of fat-liquor may be increased a little, keeping the proportion of the ingredients. The dyed shade becomes very black in this way of dyeing.

The original pH of fat-liquor emulsion is 7.3 and that of the exhaust fat-liquor bath is 5.

Putting out, sammying, setting, drying, etc.:

Next day, the leathers are put out in the Putting-out machine, sammed and set by hand and hung up to dry for two days. Then they are kept in pile for 2 to 3 days. The leathers are kept under moist saw dust overnight.

Staking and toggling : Next day, the leathers are staked with the staking machine and then strained in the board by iron nails or toggled and kept for one day.

Trimming, buffing, cleaning, etc.:

Next day, the leathers are taken off the board, trimmed round the edges to get the nice pattern, buffed on the flesh side, cleaned and kept ready for finishing.

Finishing :

Clearing :

Chlorozol Black E 240	..	1 oz.
Ammonia	..	8 ozs.
Methylated spirit	..	2 ozs.

Water to make one gallon.

One brush coat of this solution is applied to the grain side of the leather, dried in the shade and then in the sun or hot room for 15 minutes. Then the leathers are cold-plated at 150 Kg/Sq. cm. pressure and taken for finishing.

Preparation of season :

Pigment : Earnshaw bright black pigment

powder	..	1 part.
Water	..	3 parts.

The pigment powder is soaked in water and then heated over water-bath for half an hour.

Casein Solution I:

Casein	..	1 part.
Borax	..	¼ part.
Water to make 10 parts.		

Casein is soaked in Borax solution for 2 hours and then heated over water bath for ½ an hour to get it well dissolved.

Shellac solution:

Shellac	..	1 part.	Dissolved by heating over water-bath.
Borax	..	¼ part.	
Water to make 10 parts.			

Gelatin solution:

Gelatine	..	1 part.	} Soaked and dissolved by heating over water-bath.
Water to make			
upto	..	10 parts.	

Wax solution:

Carnauba wax	..	1 part.	Wax is melted and hot soap solution is added and heating is continued till homogeneous smooth mass is obtained.
Soap	..	¾ part.	
Water to make upto 10 parts.			

Binder:

Casein solution	..	25 parts.
Shellac solution	..	5 „
Gelatine solution	..	10 „
Carnauba wax emulsion	..	2½ „
50% T.R.O.	..	5 „
Nitrobenzene	..	4 „
		51½ parts.

Two parts stock binder and eight parts water should be mixed when used in the season.

Nigrosine solution:

Nigrosine	..	2½ parts.
Water	..	97½ „
		100 „

Casein Solution II:

Casein	..	1 part.
Ammonia	..	⅓ to ¼ part.
Water to make up to 10 parts.		

Season:

Pigment	..	2½ parts.
Casein solution I	..	10 „
Binder solution	..	10 „
Nigrosine solution	..	100 „
Ox-blood	..	5 „
Diethylene glycol	..	1 „

They are mixed together one after another and then 2 parts formalin mixed with 20 parts water are added slowly to it while stirring the same. Then, the whole volume is made upto 160 parts.

Two coats of this season is applied to the grain side by brush and another spray coat after diluting the season as follows:

Above season	..	1 part.
Casein Solution II	..	⅛ „
Formalin (10%)	..	⅛ „
Ox-blood	..	¼ „
Milk	..	⅓ „
Water	..	4 „

The leathers are dried well, glazed and kept in pile for one day. Next day, the leathers are ironed (hot), first by heavy iron and then by light iron, assorted or graded and thus finished.

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TECHNICAL SEMINAR

Effect of staling on the nature of salt absorption during wet salting of hide.*

S. C. NANDY

It has been suggested by a number of investigators that if a hide is to retain the conditions of a fresh one it should not be allowed to stale for more than a few hours after the death of the animal. In order to determine to what extent such staling interferes with the usual process of curing, a study has been made on the nature of salt absorption during brining and salting of hides. The following observations have been made :

(a) The amount of final salt absorption at the end of 24 hours brine treatment at 30°C is fairly constant upto a staling period of about 24 hours but, with prolonged staling the final salt absorption appears to be comparatively greater.

(b) The rate of salt absorption increases rapidly with the period of brine treatment and practically reaches the maximum within about 12 hours and then increases slowly to some slight extent.

(c) The rate of salt absorption during initial period of brining differs appreciably with the staling period. The salt absorption decreases progressively as the staling period increases, but as the staling period exceeds 8-10 hours, the salt absorption again increases gradually and after about 20 hours of staling, the salt absorption almost becomes the same as that of the fresh hide. With a further increase, in staling period, the salt absorption also slightly increases. A

*Summary of the Seminar talk delivered on 18th October, 1957.

similar nature of salt absorption is found even in the case of initial salting. This gives a very clear indication of the nature of salt absorption with increasing staling period and will probably throw light on this controversial point of the effect of staling on salt absorption. The findings of both McLaughlin and Theis and also Stather and Herfeld are thus confirmed.

(d) Further investigations show that the rate of dehydration is directly proportional to the rate of salt absorption and this holds good upto a staling period of about 30 hours, beyond which, this relation does not hold good.

(e) The effect of staling on the nature of brine drainage during salting was also determined. Independent of the staling period, the rate of brine drainage is very rapid during the early hours of salting and the brine is almost completely drained, within 24 hours under the experimental conditions. The quantity of brine drained greatly diminishes as the staling period increases. This indicates that a highly staled hide retains more water leading to a delay in dehydration.

CLASSIFIED ABSTRACTS

PROCESSES PRIOR TO TANNING

DIFFERENTIATION BETWEEN BREAKDOWN PRODUCTS OF COLLAGEN AND KERATIN IN LIME LIQUORS. D. Wegerle and H. Zahn, *Leder* 6, 298-304 (1955) via *J. Appl. Chem.*, 7, 2, i-130 (1957).—The lime liquor is filtered and dialyzed, protein is ptd. by acid, filtered and hydrolyzed. The hydrolyzate is examined by paper chromatography. Depending upon the relative quantities present of serine, glycine, cysteic acid and hydroxyproline, it is possible to determine whether the lime liquor contained chiefly breakdown products of keratin or collagen.

STUDIES ON HAIR ROOT. A. Küntzel and T. Stirtz. *Das Leder* 8, 9, 211 (1957).—Both in keratolysis and enzymic unhairing hair loosening commences with an attack on the outer root sheath, and is continued by the swelling and breakdown of the inner root sheath and parts of the hair that are not keratinised. Papilla hairs, club hairs, and new hairs are affected similarly. Short hairs, that project only slightly from the epidermis, are not efficiently removed by the unhairing machine. The inefficient removal of hair root remains on scudding leads to leather defects in cases where pigmented hair roots or pigmented new hairs are concerned.

ON "NON SWELLING" ACIDS. G. Otto. *Das Leder*, 8, 5, 100 (1957). The behaviour of various sulphonic acids is discussed, whose behaviour towards hide substance occupies a mean position between acids that swell and those that tan. Technical possibilities of using such acids in tanning is discussed.

VEGETABLE TANNING

INVESTIGATIONS ON LEAF TANNING MATERIALS 1. THE HEAT LIABILITY OF THE SUMACH TANNINS. G. Vágó, *Das Leder*, 8, 5, 110 (1957).—Indian sumach (*Rhus cotinus*) contains tannins of differing quantity and quality in the leaves, bark, and wood. For technical purposes, the heat-labile leaf tannin is only of interest from the point of view of yield. The relations be-

tween the different types of tannins is discussed from the aspect of plant physiology.

ON CHEBULAGIC ACID AND CHEBULINIC ACID. Otto. Th. Schmidt. *Das Leder*, 8, 5, 106 (1957).—Chebulagic acid ($C_{41}H_{30}O_{27}$) and chebulinic acid ($C_{41}H_{32}O_{27}$) in the initial stages of hydrolysis take up water and are converted into new compounds, neochebulagic acid ($C_{41}H_{32}O_{28}$) and neochebulinic acid ($C_{41}H_{34}O_{28}$), which contain the original structural units. Study of the neo-acids, particularly their breakdown on methylation, shows that in chebulagic and chebulinic acids the chebulic acid ($C_{14}H_{12}O_{11}$) unit is connected by two bonds to the 3 and 4 hydroxyls of glucose. On hydrolysis, Chebulic acid is the first unit split off. In this way, from chebulinic acid is produced 1,3,6, trigalloyl- β -D-glucose, which is an analogue of corilagin (1-galloyl-3,6-hexahydroxy-diphenoyl- β -D-glucose). Structural formulae are proposed for chebulagic and chebulinic acids, as well as for the two "neo" acids. Experiments are described to show the occurrence of hexahydroxy-diphenic acids in the ellagic tanning materials.

ON THE CHEMISTRY OF TANNINS OF SPRUCE BARK—IV. COMMUNICATION. Horst Endres. *Das Leder*, 8, 9, 222 (1957).—From the inner bark (cambium) of fresh spruce bark a mixture of different tannin-like glucosides was extracted with ethyl acetate under conditions which excluded oxidative changes; from this mixture, a crystalline glucoside was separated chromatographically. The corresponding crystalline aglucone was also isolated by fermentative removal of sugar, and its structure largely determined. It is clear that the basic structure is not of a catechin type but is far more based upon an oxystilbene configuration.

OTHER TANNAGES

BASIC PRINCIPLES FOR THE PREPARATION OF AROMATIC SYNTANS—I. RAW MATERIALS AND METHODS. *Das Leder*, 8, 9, 229 (1957).—The basic principles have been laid down for methods of preparation of aromatic syntans based upon the three usual methods of solubilization of aromatics, oxyaryl compounds, and their condensation products. These three methods are: sulphonation with sulphuric acid; sulphomethylation (condensation with formaldehyde and bisulphite); and amphotericisation (condensation with basic groups). In cases of sulphuric acid sulphonation, distinction is made between (1) condensation

or the sulphonic acids of aromatic basic substances; (2) sulphonation of novolaks; and (3) mixed condensation.

TESTING

ASSAY OF SODIUM HYDROSULFITE. *Am. Dyestuff Reporter*, 46, 12, 443 (1957).—A number of available methods were reviewed and the iodine formaldehyde method is recommended because of its simplicity.

Y. N.

A CHROMATOGRAPHIC METHOD FOR THE IDENTIFICATION OF AMINO ALDEHYDE FINISHES ON TEXTILES. *B. Norwick and Erwin Bierig Am. Dyestuff Reporter*, 46, 9, 314 (1957).—Descending paper chromatographic technique is described.

Y. N.

A RAPID TEST FOR RESIN IDENTIFICATION ON TEXTILES. *John H. Howard. Am. Dyestuff Reporter*, 46, 9, 313 (1957).—A rapid method based on acid hydrolysis of the aminoplast resin followed by treatment with Sodium Hydroxide to identify urea formaldehyde resins is described. The acid hydrolysed resin, when treated with phenyl-hydrazine and ferric chloride forms a colour characteristic of the particular resin.

Y. N.

HEAT AND PERSPIRATION RESISTANCE OF INSOLE LEATHER. *G. Vágó and K. Fekete, Das Leder*, 8, 6, 137 (1957).—The resistance of insole leather to heat and perspiration is improved by various combination tannages. Good results can be obtained by retannage with formaldehyde and aluminium sulphate. Aluminium salts are used with pyrogallol tannins, and formaldehyde with condensed tannins. Temperature conditions during the hot-moulded process were investigated, and rapid tests for resistance to heat and perspiration proposed.

INVESTIGATION ON ELASTICITY OF LEATHER. *G. Tóth and V. Posa Das Leder*, 8, 7, 173 (1957).—The firmness of leather is best represented by the bending modulus E . Hooke's law only holds good for small deflections; for larger deflections, the curve relating load and deflection flattens out. The maximum

is attained when the end of the sample is deflected through 90°. The bending force increases as the cube of the leather thickness. With maximum bending, there is a quadratic relation between load and deflection. Leather varies in many ways from the behaviour of a homogeneous and completely elastic substance. Under the same load conditions, deflections from the grain and flesh sides differ. On bending a sample several times, relaxation and hysteresis occur. The value of E alters with changes of density of the fibre structure.

COLORIMETRIC DETERMINATION OF TYROSINE. *G. Ceriotti and L. Spandrio. Biochem. J.* 66, 4, 607, (1957).—An improved method for the quantitative determination of tyrosine by the Gerngross-Voss-Herfeld (1933) reaction is described. Optimum experimental conditions were selected. The solution of α -nitroso- β -naphthol was made in aqueous 0.1 N-Sodium hydroxide. The exclusion of ethanol from the reaction allowed stabilisation of the colour. Linearity of colour response was obtained with solutions containing between 1 and 16 μ g of tyrosine 1 ml. The method can be used to estimate the tyrosine content of proteins.

pH IN LEATHER MAKING. *H. G. Turley. J.A.L.C.A.*, 52, 7, 354 (1957).—The significance of the pH value of the skin fibres, as opposed to the pH of the liquor is emphasised. Examples are cited where the external solutions—bate liquors, pickle liquors, or vegetable tan liquors—may have the same pH value but where the character of the leather may be affected radically by differences in pH value in the interior of the pelt.

CREEP RUPTURE OF LEATHER UNDER TENSILE LOADS. *Donald H. Russel. J.A.L.C.A.*, 52, 7, 396, (1957).—Certain dumbbell-shaped tensile strength specimens of leathers show a type of creep rupture or static fatigue when subjected to static tensile loads close to their ultimate strength. Studies made at the Franklin Institute show that the static fatigue life of leather decreases as the load increases, and increases with leather thickness. Holding leathers under relatively low tension (static loads), especially in the minimum stretch direction, was found to produce increased static fatigue life, apparently due to fiber orientation.

A METHOD FOR THE RAPID DETERMINATION OF CALCIUM IN PELT. *A. Stehlik and M. Podolska. Kozarstvi*, 6, 162-163 (1957) *Via J.A.L.C.A.*, 52, 7, 405, (1957).—Calcium is

determined colorimetrically with pyrogallol-carbonic acid, which produces a blue color. The determination is possible by using standards containing 0.2 to 1.0 mg. Ca in 10 ml. without using a photocolormeter. Prisms 2 to 4 mm. square are cut from the pelt 5 cm. from the spine and 5 cm. from the root of the tail. A 2.0 g. sample is hydrolyzed by boiling for 5 min. in 10 ml. of 0.1 N HCL. The hydrolyzate is mixed with 1 ml. of 2% starch solution, 1 ml. 2N NaOH, 1 ml. ether, and 10 ml. of a saturated solution of the reagent. The latter is made by boiling 10 g. pyrogallol for 2 hrs. with 40 g. NaHCO₃ and 70 ml. water, under reflux, cooling and acidifying with HCl. The precipitated pyrogallol-carbonic acid is filtered and recrystallized from hot water. The Ca contents of calf, goat and steer hide at the stages indicated, were found to be: untreated 0.3, 0.5, 0.35%, after deliming 0.22, 0.3, 0.15%, after bating 0.15, 0.2, 0.15%.

ACTION OF PERSPIRATION ON VEGETABLE TANNED LEATHERS. R. Ferebauer, *Kozarstvi*, 6, 34-36, 54-55 (1956) via *J.A.L.C.A.*, 52, 7, 406, (1957).—Action of perspiration on vegetable tanned insoles was studied. The pH value of fresh human perspiration is 5.2-6.0, but that of perspiration extracted from socks worn 5 days is 6.6-8.7. The most effective artificial perspiration contained 0.05 N NH₄OH, 0.4% NaCl, and 0.05% α -amino-caproic acid. Chemical analyses of insoles worn for 4, 8, and 10 months are given. Ash content increased from 1.5 to 3.6% and pH value from 4.86 to 5.80, and tear strength decreased from 2.6 to 1.4 kg. per sq. mm. Surface shrinkage occurs as a result of repeated wetting by perspiration or by water at 37°C, and drying. Maximum longitudinal shrinkage after treatment with artificial perspiration for 35 days is 12.4 mm. Prechroming of vegetable tanned insoles does not influence the deterioration.

INVESTIGATIONS OF SYNTHETIC AGENTS BY PAPER CHROMATOGRAPHY. G. Vágó and I. Molovecz, *Acta, Chim. hung.* 10, 169-178 (1956) via *J. Appd. Chem.* 7, 4, i-298 (1957).—Rutter's method of ring chromatography is suitable for investigating synthetic tanning agents (condensation products of CH₂O with sulphonated phenols, polyhydric phenols or naphthols). A 116 mm. diameter paper is supported horizontally between two Petri dishes with a tongue hanging down into the eluant composed of butanol-acetic acid-water (4:1:5) and 0.005 ml. of sample is placed in the centre. Stabilised diazo compounds of 4-benzamido-2-methoxy-5-methylaniline and similar bodies, and p-aromatic diamines such

as N-diethyl-p-phenylenediamine, are better developers than FeCl₃. In general, R_F values decrease with increasing hydrophilic properties and increasing mol. wt. Chromatography makes it possible to distinguish various components with different degrees of sulphonation and condensation, and to identify or distinguish between different tanning agents.

SOME NOTES UPON HIDE AND LEATHER QUALITY INTERRELATIONSHIPS. Raymond Hauck and Robert M. Lollar. *J.A.L.C.A.*, 52, 7, 361, (1957).—Two hundred sides of chrome-tanned side leather and the hides from which they were made have been examined to secure information on the contribution of various characteristics of the cured hide to the quality of the leather. Despite the sensitivity of a paired-side experiment in which alternate sides of the same hides were subjected to saltcuring before and after a 48-hour post-mortem delay at 65°-70°F. no significant difference was noted in the hide inspector's evaluation of the cured sides or in the leather inspector's evaluation of the final leather. The most significant factor for contributing to the physical properties of the leathers was their content of hide substance, and it is suggested that tanners should be more concerned about the content of leather-making substance in the hide lots which they purchase. It should not be generalized from these experimental results that careless practices in the handling of flayed hides during curing and storage cannot produce undesirable results observable in the quality of the final leather. It is, however, emphasised that the estimation of the leather-making potential of a lot of cured hides is a very complex subject, and it is hoped that the publication of this article will stimulate further thinking and study of the subject so that adequate quality control specifications on cured hides can be written at a later date.

THE VOLUMETRIC DETERMINATION OF SULPHATE USING A HIGH-FREQUENCY CONDUCTIMETRIC METHOD. G. R. Jamieson. *J. Appd. Chem.* 7, 2, 81 (1957).—The direct titration of sulphate using a high-frequency is described. A comparison is made of barium acetate, lead nitrate, octa-amino- μ -amino- μ -nitrodicobaltic tetranitrate and hexa-aminocobaltic bromide as precipitants for sulphate in the range 2-20 mg. SO₄²⁻. It is shown that nitrate ion interferes by giving high results when barium acetate is the titrant. Chloride ion does not affect the results when any of the above compounds are used as titrants.

A LABORATORY METHOD FOR MEASURING EFFECTS OF PROCESS VARIABLES ON LEATHER QUALITY. 1. SELECTION OF SAMPLES FOR LABORATORY EXPERIMENTS. *Herbert J. Hodus and Robert Stubbings. J.A.L.C.A., 52, 8, (1957).*—Samples for experimental studies of leather process variables may be chosen in many different ways, such as random samples from a single side or skin, random samples from one general area of a single skin, random samples from the same area of many hides or skins, paired samples taken immediately adjacent to each other, paired samples taken from the same areas of the right and left sides of the skin, and various Latin and Graeco-Latin square sampling from a large area of a single skin. These methods have been carefully studied statistically in order to find out which methods are most sensitive and most reliable for evaluating the effects of process changes. By far the best sampling method turned out to be matched pairs chosen symmetrically with respect to the backbone and taken either from many areas of a single hide or skin or from many hides or skins. At least 20 pairs of samples must be taken precisely symmetrical to the backbone, individually marked for later identification, and divided into an experimental and control lot by some prearranged plan whereby both control and experiment contain equal numbers of rights and lefts. The pairs can be selected in several ways with little effect on the reliability of the results, i.e. cut from the same position of many hides, cut from many positions on one hide, or any combination of these. The choice of the positions to be used depends upon the experimental variable being studied and upon the interpretation to be placed on the results. II. LABORATORY-SCALE EXPERIMENTS AND ASSESSMENT OF LEATHER QUALITY* *Herbert J. Hodus and Robert Stubbings. Ibid., 52, 8, (1957).*—A machine for duplicating the action of large-scale tannery drums on small hide pieces was developed, depending mainly upon a high-speed vertical oscillatory motion but also including provisions for adding reagents while shaking, continuous throughout washing at controlled temperature and rate of flow, and externally regulated heating or cooling. A staking machine and photometric area-measuring machine were also developed for use with small samples. Two series of tests were run using the laboratory method described above: one with the basicity of the chrome liquor as the variable, and the other with the pH of neutralization following chrome tannage as the variable. The results of these small-scale tests were compared

with full-scale tannery tests of the same variables, and the results in terms of break and temper of the leather agreed relatively closely with the tannery results.

METHODS FOR DETERMINING THE DEGREE OF FINE-NESS OF HIDE POWDER. *H. J. Kuerth. Das Leder, 8, 3, 49, (1957).*—The quality of any hide powder is mainly dependent on its degree of fineness. It is especially true when the hide powder is to be used for filter analysis. Different methods for determining the degree of fineness are studied as to their suitability for the purpose. The measurement of the permeability of a layer of hide powder of predetermined weight and thickness to air was found to be a simple and at the same time most sensitive method. Two methods suitable for this measurement are described.

IMPROVED PROCEDURES FOR LOEWENTHAL OXYDIMETRIC METHOD OF ESTIMATING TANNINS. *B. Glozie. Das Leder, 8, 3, 57 (1957).*—Modifications of the well known Loewenthal method of tannin estimation are suggested, so that the analysis may be conducted without reference to gallic acid. In one instance the author recommends the titration of the tannin with N/50 permanganate solution using indigo carmine as indicator. In another the use of indigo carmine is avoided and here the unused excess permanganate solution is back titrated. By adopting this method "Permanganate values" are determined, and standardised against hide powder-tannin analyses that are conducted at the same time with the corresponding tanning material.

THE PAPERCHROMATOGRAPHIC INVESTIGATION OF SYNTHETIC TANNINS. *G. Vágó and I. Molovecz. Das Leder, 8, 4, 81 (1957).*—The Rutter method of ring-paperchromatographie gives satisfying results when applied in the investigation of synthetic tanning materials. The spots were developed by a mixture of n-butanol, acetic acid and water and sprayed by stabilized diazo-compounds and aromatic p-p'-Diamins. Thus it was possible, to elucidate numerous syntans, till now unexplored, i.e. products derived from Naphthalin. The single components are lined up in the pattern of the ring-chromatograph according to their hydrophilic properties. Some syntans can be identified even in amounts <1 mg.

RHEOLOGICAL PROPERTIES OF SOME POLYMERIZED OILS. *T. Nakagawa and M. Seno. Bull. Chem. Soc. Japan, 29, 471-*

479 (1956) via *J. Appd. Chem.* 7, 2, i-148 (1957).—A method for measuring the dynamic visco-elasticity of liquids by torsional oscillation is described and used to study the oils produced by thermal polymerisation of linseed oil to various degrees. The amplitude effect of the dynamic properties is negligible. Very low frequencies (period 10 sec.—5 min.) were used. The temp.-dependence of the dynamic viscosity is discussed and the Weissenberg effect tested qualitatively.

INFLUENCE OF TYPE AND AMOUNT OF PIGMENT ON PERMEABILITY OF PAINT FILMS. H. Berger (*Dtsch. Farben Z.*, 10, 211-215, 243-257 (1956) via *J. Appd. Chem.*, 7, 2, i-148 (1957).—The porosity, true and apparent swelling and permeability of the films in 0.01 N-HCl have been measured by indicator, gravimetric and conductivity methods, respectively. The effects of electrolyte concn., film thickness and straining of the paints were examined in preliminary experiments. The media used were chlorinated rubber, polyvinyl chloride-isobutyl ether polymethyl metacrylate, linseed oil, linseed stand oil, polyvinyl acetate and a plasticised urea resin and these were pigmented with 0-100% of pigment. The results are presented.

QUANTITATIVE ESTIMATION OF UREA AND MELAMINE IN MIXTURES OF UREA AND MELAMINE-FORMALDEHYDE CONDENSATES. G. Widmer, *Kunststoffe*, 46, 359-363 (1956) via *J. Appd. Chem.* 7, 2, i-141 (1957).—The methods described are based on ammonolysis, with liberation of urea and melamine, followed by formation of dibenzylurea and melamine picrate for gravimetric estimation. Various modifications of technique are described for use in presence of fillers or of lacquer resins. The methods are suitable for process control. (7 references).

THEORIES

ON THE QUESTION OF THE EXISTENCE OF RETICULIN IN ANIMAL HIDE (*Critical review of the new literature*). A. Kuntzel, *Das Leder*, 8, 4, 73 (1957).—In the corium area of the skin there are two types of connective tissues; collagen and elastin, the difference being mainly histochemically. A third type of connective tissue, "reticulin", is not existent. Those parts of the skin, which are defined as "reticular tissue", are in fact collagen derivating morphologically. The introduction of the word reticulin or reticular tissue in the description of connective tissue of

the skin has recently given cause to considerable confusion. [Reticulin mistaken as elastin respective soluble collagen (procollagen)]. The object of this paper is to clarify and correct these mistakes.

THE AMINO ACID COMPOSITION OF FISH COLLAGEN AND GELATIN. J. A. Eastoe, *Biochem. J.* 65, 2, 363 (1957).—The amino acid compositions of collagens and derived gelatins from sturgeon, cod, the shark (*selachus Maximus*) and the Australian lung fish have been determined. These fish collagens show a similar amino acid distribution to mammalian collagen, with decreased amounts of proline and hydroxyproline and increased serine, threonine and in some cases, methionine and hydroxylysine. Gelatin prepared from cod bone has a very low rigidity at 10, whereas sturgeon, shark and lung-fish collagens give rise to gelatins having rigidities of the same order as, but probably somewhat below, those of mammalian gelatins. In general, the shrinkage temperature of the collagen and gel properties of extracted gelatin decrease with decreasing hydroxyproline content. Certain departures in detail from this behaviour indicate that other unknown features of composition may influence the stability of linkages between polypeptide chains. Variations in the properties and compositions of fish collagens seem to be related to the water temperatures of the normal habitat, rather than to considerations of broad zoological classification.

EVIDENCE OF A NEW COMPOUND. (lanthionine sulphoxide) in products from animal skin. H. Zahn and D. Wegerle, *Leder*, 6, 278-79 (1955) Via *J. Appd. Chem.* 7, 2, i-130. (1957).—By chromatography of gelatin hydrolyzate, a weak ninhydrin-positive spot was found, not previously identified. Evidence is given to indicate that it is due to lanthionine sulphoxide, this is thought to be produced by the action of alkali and oxygen on protein containing cystine.

CONNECTIVE TISSUE GROWTH STIMULATED BY CARRAGEENIN. 1. THE FORMATION AND REMOVAL OF COLLAGEN. D. S. Jackson, *Biochem. J.* 65, 2, 277 (1957).—1. Subcutaneous injection of carrageenin into guinea pigs stimulates the formation of new connective tissue which is resorbed after 4-6 weeks. 2. The change in concentration with time of neutral-salt-soluble collagen acid soluble collagen and insoluble collagen and the incorporation of $\alpha^{14}\text{C}$ glycine into these collagens, have been studied. 3. Maxi-

mum wet weight of new tissue is produced between the seventh and ninth day and disappears after 4-6 weeks, although the total concentration of collagen in the tissue does not reach a maximum until the fourteenth day. 4. Most of the insoluble collagen is formed between the fifth and ninth day. Neutral-salt-soluble collagen appears before acid-soluble collagen, the concentration increasing up to the fifth day, remaining constant and then increasing rapidly as the tissue is resorbed. The concentration of acid-soluble collagen increases throughout the experimental period. 5. The highest specific activity is found in neutral-salt-soluble collagen maximum activity occurring at 10 hr. with a half-life of 18-20 hr. The activity-time curves of acid-soluble collagen and insoluble collagen are similar, maximum activity occurring at 12 and 24 hr. respectively and being very much lower than the activity of neutral-salt-soluble collagen. 6. It is concluded that neutral-salt-soluble collagen is the precursor of collagen fibres and can either be transformed into acid-soluble collagen or add on to pre-existing acid-soluble collagen and insoluble collagen. 7. A water-soluble protein containing hydroxyproline has also been found.

PHASE EQUILIBRIUM IN THE HYDROTHERMAL SHRINKAGE. J. F. M. Oth, E. T. Dumitru, O. K. Spurr, and P. J. Flory, *J. A. C. S.*, **79**, 3288, (1957).—The temperature for the onset of shrinkage is shown to be substantially higher than that required for equilibrium between crystalline and amorphous phases.

A COLOUR REACTION OF FLAVANONOLS. H. Pacheco and M. Chadenson.—*Through Anal. Abst.*, **4**, 6, 1884 (1957).—Flavanonols, acetylated in boiling acetic anhydride with anhydrous sodium acetate gives bright compounds. These treated with Hydrochloric acid are converted into red pigments with the characteristics of flavylum chlorides, which is specific to flavanonols. Their spectrum shows a band between 510 and 545 mμ.

GENERAL

MECHANISATION OF THE TANNING INDUSTRY. A. Kuzmin, *Director of the Thaelmann Tanning Plant, Moscow, The Tanner*, **11**, 10, 19 (1957).—The automatised Tanning Plant at Moscow makes use of radically changed conveyer. The vertical continuous and the horizontal-continuous conveyers are used. The soaking and liming of skins are proposed to be done automatically

in a hermetically sealed wooden drum 13.5 meters long and 3 meters in diameter consisting of 6 sections. An overhead travelling crane lowers three tons of the hide into this drum which rocks periodically. According to schedule the drum gives a half-turn and the first batch of the skins is automatically moved to the next section while the next batch of the skins is loaded into the soaking compartment. After treatment in this drum, the goods are moved into a general conveyer with hooks which will remove wool, flesh and hair and clean them. The flesh is removed pneumatically. For fleshing, cleaning and setting, etc., the belt type of conveyer is used; for shaving, sorting and dyeing of chrome leathers, the plastic conveyer is used. The leather finishing is done by an automatic machine.

Y. N.

LEATHER & ENGINEERING. Henry H. Beakbane, *L.T.R.* **124**, 3713, 391 (1957).—The Engineer is constantly looking for materials with new properties. An aircraft designer requires flexible materials that maintain physical properties for a long period over a wide range of temperatures and in the presence of corrosive materials. The ship builder requires a flexible water proof material that will withstand the rotting effects of sea water and rusting iron. The Civil Engineer uses packings, diaphragms and trunking under the most arduous conditions in the presence of dirt, dust and water. The industrial instrument manufacturer requires dampers, seals and diaphragms in a resilient material. Hydraulic systems require packings and seals. It is evident that the Leather Industry could sell more leather to the Engineer if only it exerted itself.

Y. N.

LEATHER BOARD AND ITS USE IN THE SHOE INDUSTRY A. J. M. Draper, *Proc. Tech. Sec. on Brit. Paper & Board Makers' Assoc.* **38**, Pt. 1, 133 (1957).—An account is given of the various types of leatherboard and the materials used in their manufacture, with particular reference to those less familiar to the papermaker. The various methods of shoe construction are described and the part played by leatherboard in shoe construction discussed. Some methods used in testing leatherboard are given.

SOME CHARACTERISTICS OF EPOXIDE RESIN SYSTEMS. E. J. Allen and W. M. Hunter, *J. Appd. Chem.* **7**, 2, 86

(1957).—A discussion is given of the hardening of epoxide resins with amines and of methods of modifying polyfunctional aliphatic amines to widen their range of application. The effects of time and temperature of curing of epoxide resin-amine systems on the properties of the products are briefly discussed.

A REPORT ON THE CONSTRUCTION AND OPERATION OF CLARIFICATION PLANT IN TANNERY. *L. Feikes and E. Roth, Das Leder*, 8, 5, 114 (1957).—This paper is a report of preparations for, construction of, and operation of a clarification plant for tannery effluent. Much water is used in the tannery, and receives various, typical impurities. Such effluent contains sulphides and considerable amounts of skin and hair protein, which is mostly alkaline. Experiments are described in which these impurities are precipitated from the water by means of ferric sulphate and bicarbonate. A plant operating on this principle is illustrated and described.

NOTES & NEWS

SYNTHETIC TANNIN FROM RIVER WASTES

Ontario Research Foundation of Toronto has developed a synthetic tanning agent using river polluting industrial wastes, and believed to be less expensive than present natural materials. Experiments recently carried out have shown that sulphite liquor, a waste product of the pulp and paper industry, can be broken down into two fractions, one of which contains the necessary chemical ingredients for leather making. Heretofore these elements have been discovered before found in Tannin. Other synthetic agents have been discovered before, but were far too costly for commercial uses. Now chemists have found that by the addition of Phenol, the sulphite liquor fractions can be made to do the job. Cresol, a by-product of the oil industry, can also be used, but is somewhat more expensive.

—*Lea & Shoes*. 133, 20, 16 (1957).

LEATHER COLOURS FOR NEXT SPRING AND SUMMER

The British Colour Council have now issued a range of 15 colours for Spring and Summer 1958. These colours for shoes, gloves, handbags and other leather accessories are coordinated with the dress and millinery colours, and reflect the present trend for clear, clean colours in woven and printed fabrics. The colours shown on the card are: Orange delight, orange lily, Misty green, Otago green, tuquoisetoned carnival blue, Seaspray, Galway grey, Misty blue, Curzon blue, New Laurel, Germanium pink, Cinnamon, Elegano Beige, Highway Tan, Rose Beige, Peach Blossom and Gull grey *L.T.R.* 125, 3727, 407 (1957).

TOUCH UP KIT

The Bullows V 257 touch-up kit is intended to meet a need for a compact portable unit which allows a range of colours to be sprayed easily by one operator, with a minimum loss of time in changing colours. It incorporates a L/910 Spray Gun with seven aluminium cups of 5 oz. capacity, six cups being used for colours

and one for thinners. There is a built-in reducing valve, a suitable length of hose, and the whole kit is mounted on a caster-based trolley.—*L.T.R.* 124, 3716, 510 (1957).

E.-J. LAUNCHES \$100,000 SOLVENT TANNING STUDY

Endicott-Johnson Corp. will invest a total of \$100,000 in a research program aimed at developing a new solvent tanning process designed to replace the traditional water process, according to Raymond A. Mills, Vice-President and General Manager. The company is now building a pilot plant in Endicott, N. Y., where the research program will be conducted. Mills said plans call for the program to get underway within the next 30-60 days but it will be "a year or two" before anything conclusive is known. And it might take four or five years before the company is able to switch over to the new process. If successful the solvent process would have a tremendous impact upon Endicott-Johnson's interceptor sewer-treatment plant program, Mills said. The company would be able to reclaim the solvent and thus reduce or eliminate most of the liquid waste it now disposes of through city sewers.

—*Lea & Shoes.* 134, 7, 12 (1957).

RESEARCH BEARS FRUIT

Practical Demonstration No. 9

Process: Manufacture of Fancy Leathers.

Period: 18th November to 25th November 1957.

Place: Central Leather Research Institute.

In order to diffuse the results of scientific research into the industry every month, a process for the manufacture of a new type of leather is demonstrated at the Central Leather Research Institute to the tanning trade. The tanner is in a position to see for himself the process details from the raw material to the finished product and to assess the quality and the economics of making this product. The 9th in this series of practical demonstrations is to be conducted during November 1957 and the processes to be demonstrated are on the manufacture of a variety of fancy leathers.

There are various methods for decorating a piece of leather so as to increase its sale value. The rejection leathers, and splits

that fetch a low price could be processed into a variety of fancy leathers. This may be done by colouring and printing or by transfer prints, by textile block printing and marbling by sponges.

The above mentioned processes will be demonstrated to the Industry from the 18th of November 1957 to the 25th of November 1957. You are welcome to attend this practical demonstration and to satisfy yourself with the efficiency of the process and the necessity for you to take it up later.

Arrangements are also made as usual, at this Institute for boarding and lodging of the participants at cost. Please let us know early the name of your representative participating in the Demonstration.

C. L. R. I. NEWS

Dr. Y. Nayudamma, Assistant Director-in-charge, Central Leather Research Institute, Madras, left for Rome on September 18, 1957, to participate in the *International Conference of Leather Chemists' Societies* (Sept. 16-23, 1957). Dr. Nayudamma will also visit tanneries, Leather Research institutes and leather auxiliaries manufacturing concerns in England, Italy and West Germany during his six weeks' tour.

Dr. S. K. Barat, Senior Scientific Officer, Central Leather Research Institute, is looking after the duties of Assistant Director-in-charge in the absence of Dr. Y. Nayudamma, who is away on tour abroad.

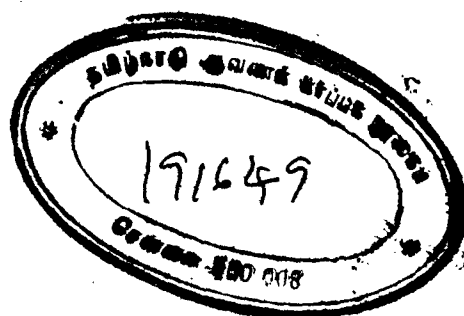
Sri R. Selvarangan, Junior Scientific Officer, Central Leather Research Institute, Madras, visited M/s. Shree Lakshmi Tannin Extract Factory, Kharagpur, at their request and investigated the various problems connected with the improvement of the colour of the Myrobalan extract.

VISITORS

<i>Name</i>	<i>Date of visit</i>
1. Shri Ramprasad, Superintendent, Industries and Commerce, Warrangal, Andhra Pradesh	19-9-1957
2. Mr. Romulad L. Lozano, Bureau of Animal Industry, Manila, Philippines	28-9-1957
3. T. M. Z. Mahamooth, Deputy Director (AH), and Chief Government Veterinary Surgeon, Ceylon	10-10-1957
4. D. W. Amarasinghe, Chief Municipal Veterinary Surgeon, Colombo	10-10-1957
5. A. Amarasinghe, Public Health Veterinary Officer, Ceylon	10-10-1957

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