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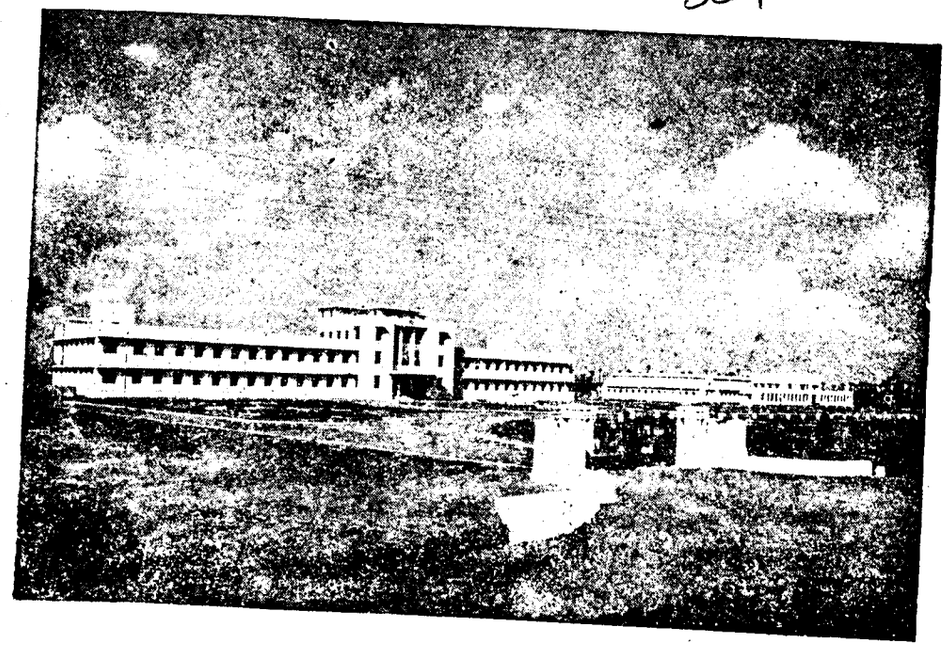

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STUDIES ON ENZYMIC UNHAIRING AND DEGREASING FOR PRODUCTION OF LEATHER *

BY

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Central Leather Research Institute, Madras

(Received on 24th Sept. 1958)

SUMMARY

Comparative chemical, physical and microscopical assessments of the quality of the leathers produced by the traditional liming process and by the two enzymic unhairing processes utilising a protease and an amylase have been made and the results obtained have been discussed.

The optimum conditions for the hydrolysis of skin lipids by castor seed lipase have been studied with respect to the effects of pH, period of digestion, temperature and enzyme concentration and degreasing experiments with lipase on sheepskins before and after enzymic unhairing have been carried out.

Liming is the traditional process of unhairing skins and hides. It has not been established whether bacterial enzymes also play any part in unhairing by liming. Although it is definitely established that bacteria cannot thrive in new lime liquors, old lime liquors may contain large numbers of active alkali-resistant bacteria. It may be expected that the action of bacterial enzymes in old lime liquors may play an important part in unhairing when liming is of long duration. However, if a sharpener is used to cut down the time of liming, there may not be sufficient time available for bacteria to grow or to play any major part in the unhairing process.

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* Part of a thesis, which formed the basis for the award of Ph.D. degree of the Madras University, to W.M.

A good deal of work has been done on the direct application of proteolytic enzymes in dehairing skins and hides. The first successful enzymic unhairing was achieved in 1910 by Rohm[1] who patented an 'Arazym' process in which pancreatic enzymes were used. Since then, a series of patents[2] have been taken on enzymic unhairing making use of proteolytic enzymes derived from plant, animal, mold and bacterial sources. It has been reported[3-5] that amylolytic enzymes also are capable of unhairing skins and hides. Making use of the latex of madar plants (*Calotropis gigantea*) and the water extract from germinated 'ragi' (*Eleusine coracana*) which were found[6] to be rich sources of protease and amylase respectively, two processes of enzymic unhairing have been developed[7, 8] for the production of different types of leather.

In the traditional liming process, the natural lipids of skins are partially saponified and removed. Although such saponification of skin lipids is not possible in the enzymic unhairing process, no special difficulty was experienced with regard to the removal of natural lipids from goat skins and cow hides, because the enzymic unhairing was found to assist scudding most effectively and to produce extremely clean pelts. However, the lipid content of sheep skins is comparatively higher than that of other skins. Several methods, *viz,* solvent extraction, emulsification, pressure process, paraffin process, etc., are known for degreasing sheep skins; however, lipolytic enzymes for degreasing have not yet been commercially exploited. It was therefore, thought interesting to study the effect of lipase on sheep skins which were unhaired by enzymic unhairing processes. It was also thought desirable first to standardise the optimum conditions for the hydrolysis of skin lipids by a lipase. In the present investigation therefore, comparative assessments of the quality of leathers produced by the two enzymic unhairing processes[7, 8] and by the liming process have been

made and the reactions of castor seed lipase on skin lipids studied.

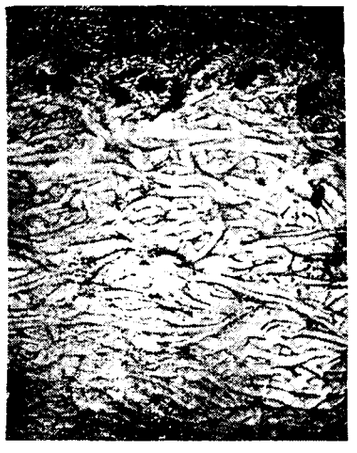
Experimental

Unhairing. One half of a skin or hide was unhaired by the liming process and the other half by one of the two enzymic unhairing processes[7, 8]. The standard liming processes as prescribed for the manufacture of glace kid, box sides, E.I. kips and skins and sole leather were followed for unhairing the control halves of skins and hides. The unhaired pelts obtained by the liming processes were delimed; the delimed pelts for preparation of glace kid and box sides, were bated in the usual manner. The unhaired pelts obtained by the enzymic unhairing processes, on the other hand, had a bated feel and appearance and hence no extra bating was required. The different samples of pelts thus obtained were subjected to microscopical examination. As a typical example, the photomicrographs of the pelts for E.I. kips are presented in Fig. I.

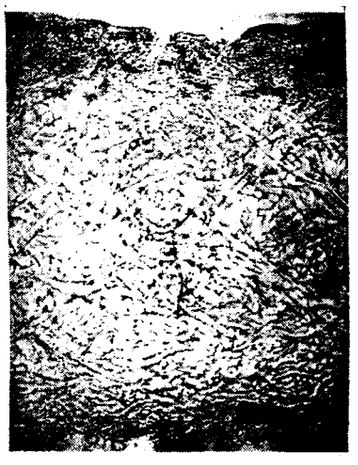
Preparation of different types of leathers: All the samples of pelts obtained by the liming process or by the enzymic unhairing processes were pickled in the usual manner. The pickled pelts for glace kid and box sides were chrome tanned by the standard two-bath process and single-bath process respectively and finished in the usual manner. The pickled pelts for E.I. kips and skins and sole leather were depickled and then vegetable tanned by following standard processes for the manufacture of such leathers.

Examination and Analysis of Leathers: Comparative assessments of the quality of the different types of leather produced by the liming process and the new enzymic unhairing processes were made with regard to general appearance, fullness, feel, tightness of grain, tear

Pelt for E.I. Kip unhaired by lime



Pelt for E.I. Kip unhaired by protease



Pelt for E.I. Kip unhaired by amylase

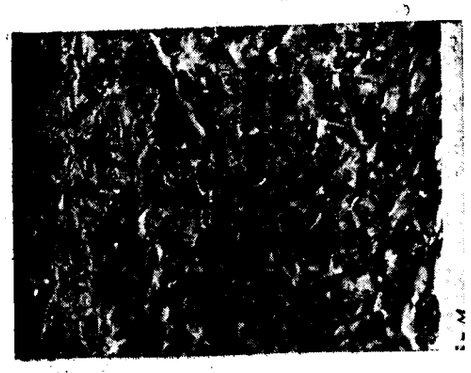
Fig. I

TABLE I

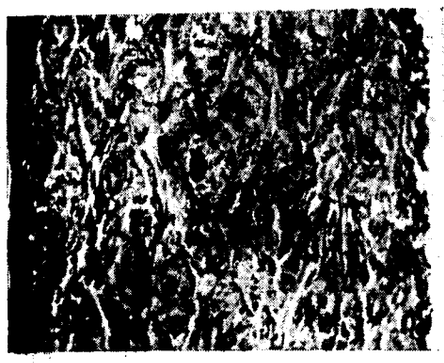
Chemical Analyses of Vegetable-tanned leathers prepared by liming and enzymic unhairing processes.

(Calculated on 14% moisture basis)

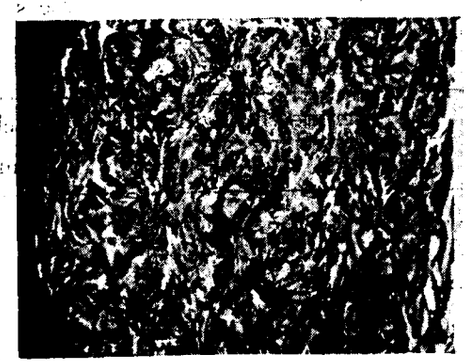
	E.I. tanned goatskin			E.I. tanned kip			Vegetable-tanned sole		
	Liming	Protease	Amylase	Liming	Protease	Amylase	Liming	Protease	Amylase
Hide substance ..	44·3	46·1	45·0	43·0	44·2	43·6	43·2	44·9	44·0
Oils and Fats ..	8·3	8·5	8·0	6·5	6·8	6·6	1·4	1·0	1·3
Water solubles ..	7·4	7·5	7·0	7·7	8·1	7·9	6·5	5·9	6·2
Ash of insolubles ..	0·1	0·08	0·12	0·12	0·1	0·1	0·35	0·41	0·38
Fixed tannins ..	25·9	23·82	25·88	28·68	26·8	27·8	34·55	33·79	34·12
Degree of tannage ..	58·46	51·68	57·5	66·7	60·6	63·7	79·9	75·2	77·5
pH of water solubles ..	4·2	4·6	4·1	4·5	4·3	4·4	3·8	3·9	4·2



Sole leather unhaired by amylase



Sole leather unhaired by protease



Sole leather unhaired by lime

Fig. II

strength and crack at double fold and under key test. All the samples of leather were then subjected to a few physical tests, standard chemical analyses and microscopical examination and photomicrographs were taken in each case. In all these analyses, care was taken in proper sampling of the pelts and leathers. As far as possible, the samples for these tests were cut from the corresponding positions of the two halves of a pelt or finished leather. Standard official methods of chemical analysis of leathers were followed. The results obtained are presented in Tables I to III. As a typical example, the photomicrographs for sole leather are presented. (Fig. II)

TABLE II

Chemical analyses of chrome tanned leathers prepared by liming and enzymic unhairing processes
(Calculated on 14% moisture basis)

	Glace Kid			Box Side		
	Liming	Protease	Amylase	Liming	Protease	Amylase
Oils & Fats ..	3·5	3·9	3·0	4·6	3·8	4·0
Cr_2O_3 ..	3·6	3·2	3·4	4·1	4·0	4·1

TABLE III

Physical testing of leathers prepared by liming process and enzymic unhairing processes

(A) Tensile Strength

Type of Leather	Tensile Strength in lbs./sq. inch		
	Liming	Protease	Amylase
Box side ..	4534	4208	4325
Glace Kid ..	4000	3840	3694
E. I. Kip ..	4150	4200	3976
E. I. tanned goat ..	1572	1605	1598
Sole leather ..	4215	4176	4045

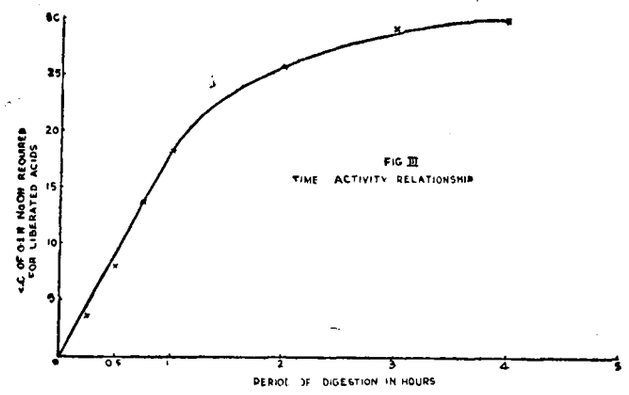
(B) Lastometer Test

Type of Leather	Liming		Protease		Amylase	
	Distension in mm.	Load in Kg.	Distension in mm.	Load in Kg.	Distension in mm.	Load in Kg.
Box side						
Crack ..	7·8	4	8·3	10	7·6	4·5
Burst ..	10·5	50	9·7	60	9·4	50
Glace Kid						
Crack ..	10·1	8·8	11·2	7·5	9·8	4·5
Burst ..	11·8	25	12·4	10	14·0	24·3
E.I. tanned goat						
Crack ..	6·7	3·5	7·1	6·1	6·4	4·7
Burst ..	8·3	7·5	—	9·0	8·1	10

Isolation of skin lipids: In order to study the optimum conditions for the hydrolysis of skin lipids by castor seed lipase, the lipids were isolated from a sheepskin which was obtained fresh from the slaughter-house. After removal of the wool by means of a razor, the skin was cut into small pieces and minced into a pulp in a mincing machine. The pulp was first dehydrated by extraction with absolute alcohol and then the residual lipids were extracted by petroleum ether (B.P. 40-60°C.) in a Soxhlet extraction assembly. The alcohol extract was concentrated by distilling off the alcohol and then extracted with petroleum ether. From the combined petroleum ether extract the lipids were recovered by removal of the solvent and finally dried under vacuum.

Preparation of castor seed lipase. The lipase was prepared in a crude but active form from fresh well-ripened castor seeds by the method of Longenecker and Haley.[9] The seeds were dehusked and macerated into a fine pulp. The oil was extracted from the pulp as completely as possible with low-boiling petroleum ether. The defatted meal was air-dried and finely powdered.

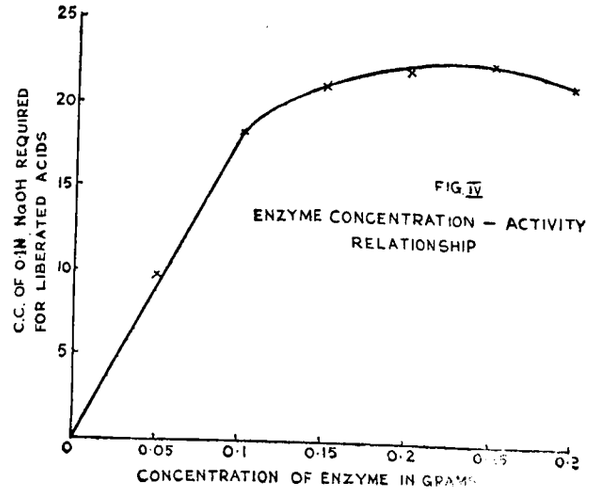
Time-activity relationship : 1 cc. portions of the lipid, 5 cc. portions of water and 1 cc. portions of sodium acetate—acetic acid buffer of pH 4·8 were triturated in a mortar and each mixture was mixed with 0·1 gm. lipase and incubated at 37°C for varying periods. At regular intervals, the digestion mixture was taken out and mixed with 25 cc. warm neutral alcohol and the contents were titrated aganst 0·1 *N* NaOH using phenolphthalein as the indicator. A blank experiment was always carried out under identical conditions using boiled enzyme solution. The activity of the lipase was expressed as the difference in the titre value for the experimental and the blank in terms of cc. of 0·1 *N* NaOH. The results are shown in Figure III.



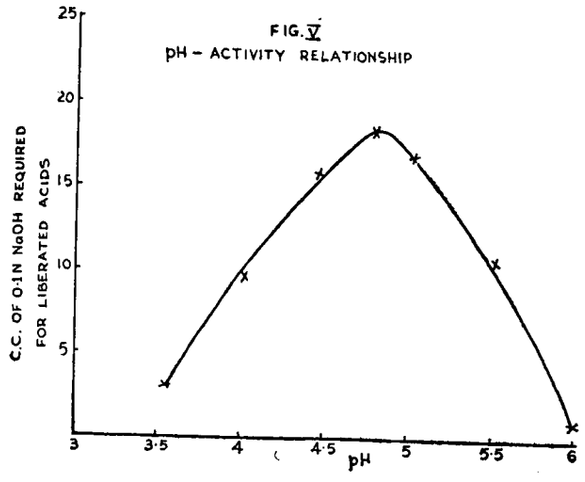
Effect of varying enzyme concentration on the lipase activity : 1 cc. portions of the lipid, 5 cc. portions of water and 1 cc. portions of sodium acetate—acetic acid buffer of pH 4·8 were used with varying proportions of the lipase and the mixtures were incubated at 37°C for one hour at the end of which the lipase activity in each case was estimated as mentioned before. The results are shown in Figure IV.

Effect of pH on the lipase activity : 1 cc. portions of the lipid, 5 cc. portions of water and 1 cc. portions of sodium acetate—acetic acid buffer of varying pH were used with

0·1 gm. portions of the lipase and the mixtures were incubated at 37°C for one hour at the end of which the lipase

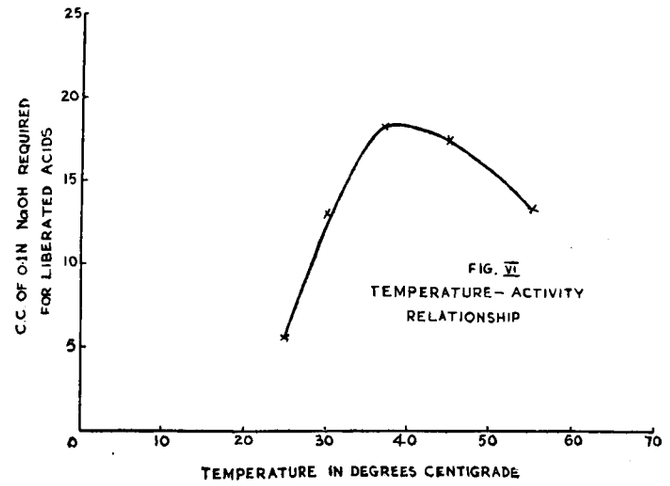


activity was estimated in each case as mentioned before. The results are presented in Figure V.



Effect of Temperature on the lipase activity: 1 cc. portions of the lipid, 5 cc. portions of water and 1 cc portions of sodium acetate—acetic acid buffer of pH 4·8 were used with 0·1 gm. portions of the lipase and the mixtures were

incubated for one hour at different temperatures and the lipase activity was estimated in each case as mentioned before. The results are presented in Figure VI.



Degreasing experiments: The initial fat content of three sheep skins which were obtained fresh from the slaughter-house was estimated. Small skin samples from which wool was closely clipped off were finely minced in a meat mincer and dried to constant weight at 50°C under vacuum. The dried material was extracted with petroleum ether (B.P. 40-60°C) in a Soxhlet apparatus for 6 hours and the fat recovered from the extract after removal of the solvent was dried to constant weight.

One skin was unhaired by the enzymic unhairing process[7] making use of the protease of madar latex. Another skin was unhaired[8] by using the amylase extract from germinated *ragi*. The small pelt samples were analysed for the fat content by the same procedure as mentioned above. The two pelts obtained after enzymic unhairing were subjected to degreasing by lipase. For this, both the pelts (about 6 lbs.) were handled for one hour in a bath containing 9 gms. lipase and required amount of water the pH of which was

adjusted to 4·8 with sufficient amount of sodium acetate-acetic acid buffer. The temperature of the bath was maintained at 37°C. The pelts were then scudded, thoroughly washed and analysed for the fat content as mentioned before. The third skin was directly subjected to degreasing by lipase in the same manner as described above. The degreased skin was analysed for the fat content in the usual manner. The results are presented in Table IV.

TABLE IV

Degreasing of skins and pelts by lipase

Treatment given	% Fat content (on dry wt. basis)		
	Sample 1	Sample 2	Sample 3
Fresh Sheepskin ..	14·3	13·2	12·1
Pelt after protease unhairing ..	13·0	—	—
Same after degreasing ..	11·9	—	—
Pelt after amylase unhairing ..	—	11·8	—
Same after degreasing ..	—	10·8	—
Fresh sheepskin after degreasing ..	—	—	9·9

Discussion

With regard to the assessment of the quality of the finished leathers from tanners' point of view, it has been observed that box sides produced by the two enzymic unhairing processes are better than the control. The feel as well as the grain of these leathers are quite similar to those of the leather produced by the usual liming process. In the case of glace kid, the leathers produced by the new unhairing processes are less smooth and somewhat weaker in

tearing strength. They are also less stretchy than the control. The E.I. tanned goatskins produced by the new methods of unhairing have the same colour as the control but have got a slightly firmer feel. The tearing strength is better in these leathers than in the leather produced by the usual liming process. The East Indian tanned kips produced by treatment with the new processes of unhairing are somewhat firmer than the one produced by the traditional liming process. In other respects they are similar to the control. Bark-tanned sole leathers obtained by the two enzymic unhairing processes are as good in appearance and as stiff in feel as the control.

The results of the chemical analyses of the different leathers as given in Tables I and II show that the leathers produced by the enzymic unhairing processes conform in general to the standard specifications laid down for such leathers. However, the degree of tannage in the case of protease unhairing has been found to be slightly lower than that of the control. The general trend of results obtained indicate that the leathers produced by the new enzymic unhairing processes compare favourably with those produced by the traditional liming process. Similar trend of results was also reported by Airoldi[10] while working on enzymic unhairing with fruits of *Solanum campylacanthum.*

As regards the physical properties also, the lastometer test and the tensile strength test indicate that the strength of the leathers produced by the enzymic unhairing processes is more or less of the same order as that of the leathers by the liming process.

The general remarks on the microscopical appearance of the pelts for East Indian tanned kips are that the grain layers of the pelts treated by protease and amylase are better than the control; it is desirable to have a little more splitting up of the fibre bundles to get a soft and pliable

leather. The leathers produced from these pelts show that the grain in both the samples of enzymic unhairing merges well into the corium which is essential in good quality E.I. kip leather. The pelts obtained by either of the enzymic unhairing processes for the manufacture of E.I. tanned goatskin indicate that further opening up of the weave, is needed for the production of good quality E.I. tanned skins. The leather produced from the pelt treated with amylase is more or less similar to the control and the leather made by treating the pelt with protease shows an open weave. The enzyme unhaired pelts, as obtained for glace kid do not show very satisfactory splitting up of the fibres and the leathers also are somewhat stiffer than the control. Although the pelts for box sides show that the grain layer is slightly firmer in the case of both the enzymic unhairing processes than for the control, the leathers prepared from them do not differ from each other and they are more or less similar to the control. In the case of sole leather, all the pelts unhaired by enzymes or by lime have a similar fibre structure, except for the angle of weave. However, in the finished sole leather, the compactness of the samples from the two enzymic unhairing processes is better than in the control.

The microscopical appearance of some pelts clearly indicate that where there is no satisfactory swelling, the opening of the fibre structure is also less satisfactory. But this is not so in the liming process. Liming not only unhairs a skin but also swells and hydrates the pelt which in turn helps the fibre structure to open up. The disadvantage of improper swelling and opening up of the fibre structure in the enzymic unhairing can be remedied if the unhairing is carried out at a slightly alkaline pH with the help of certain microbial enzymes. Or, after the unhairing by the enzymes, a short liming for a day or two may be quite sufficient for the purpose. It has been observed by Grimm[11] that in unswollen skins, enzymes may work chiefly on the layer beneath the epidermis and may not properly open up the

fibre structure, whereas, in the skins that are swollen, the fibres are properly opened up and are more accessible to the enzymes. However, Hollander[12] reported that in enzymic unhairing the pores are opened up and this helps the scud to flow out freely from the skins.

With regard to the optimum conditions for the hydrolysis of skin lipids by castor seed lipase, it has been observed that upto a maximum period of one hour, the linear relationship between time and degree of hydrolysis is maintained (Fig. III). The optimum pH for the hydrolysis of lipids by the enzyme has been found to be 4·8 (Fig. V). The optimum concentration of crude lipase preparation which is required for the hydrolysis of one cc. of lipids at a temperature of 37°C has been found to be 0·1 gm. (Fig. IV). The optimum temperature for the hydrolysis of the lipids has been found to be 37°C. At higher temperatures a sharp fall of the lipolytic activity has been observed (Fig. VI). It has also been observed that the best results with respect to the hydrolysis of skin lipids by this enzyme are obtained when the lipid is acted upon under emulsified condition. The sharp fall of lipolytic activity at temperatures higher than 37°C appear to be partly due to the fact that the stability of the lipid emulsion is affected at higher temperatures.

The degreasing experiments with sheepskins before and after enzymic unhairing have shown that under the optimum conditions of reaction, the lipids from a fresh sheepskin can be partially removed by treatment with the lipase. However, there was only slight reduction of the lipid content in the case of degreasing by lipase of the pelts which were previously unhaired by treatment with protease or amylase. It has also been observed that the grease content of the skin is slightly reduced after unhairing with protease or amylase. These results indicate that even in cases where the fat is not removed to the desired extent during the enzymic unhairing processes, an active lipase

can be used under favourable conditions for the satisfactory removal of the grease.

Acknowledgement

Our thanks are due to Dr. Y. Nayudamma, Director, Central Leather Research Institute for his keen interest in this work and kind permission to publish these results and to Mr. S. K. Mitra for the photomicrographs.

REFERENCES

1. Rohm, *German Patent* 268, 873 (1910).
2. Green, G. H., *J.S.L.T.C.*, **36**, 127 (1952).
3. Burton, D., Reed, R., and Flint, F.O., *Ibid*, 37, 82 (1953).
4 Bose, S.M., Madhavakrishna, W., and Das, B. M., *J.A.L.C.A.*, **50**, 192 (1955).
5. Cordon, T. C., *Ibid*, **50**, 270 (1955).
6. Bose, S. M. & Madhavakrishna, W., *Bull. C.L.R.I.*, **4**, 157, (1957).
7. Bose, S. M., Madhavakrishna, W. and Das, B. M., *Ind. Pat.* **50806** (1953).
8. *Idem, Ind. Pat.*, **52013** (1954).
9. Longenecker, H. E. and Haley, D. E., *J. Amer. Chem. Soc.*, **57**, 2019 (1935).
10. Airoldi, R., *J.A.L.C.A.*, **36**, 478 (1941).
11. Grimm, O., *Das Leder*, **2**, 265 (1951).
12. Hollander, C.S., *J.A.L.C.A.*, **15**, 477 (1920).

RESEARCH BEARS FRUIT

Practical Demonstration No. 3

Third Series

Manufacture of grain garment leather from E.I. Sheep skins*

BY

P. S. VENKATACHALAM & T. S. KRISHNAN

Raw materials : Prime quality E.I. sheep skins without grain defects. A weight of 6-7 lbs. per band of 12 skins and an area of not less than 5 sq. ft. per piece are preferred.

Conditioning and shaving : The E. I. skins are weighed, drawn through water and piled for 2-3 hrs. or preferably overnight, after covering them with a tarpaulin. They are then levelled to uniform thickness by shaving.

Stripping : The shaved skins are washed in a drum in 800% water for 20 minutes after which they are stripped with 400% water and 2% borax for 20 minutes. The stripped skins are washed twice in a drum in 800% water, allowing 15 minutes for each wash. The washed skins are ready for bleaching.

Bleaching : A bath is prepared as follows :

Acid Oxalic	..	1%
Calgon	..	1%
Bleaching syntan (Basyntan F.C. of B.A.S.F.)	..	2%
Water	..	400%

* Process demonstrated during March 1959.

The skins are put into the bleaching liquor and drummed for 30 minutes after which they are taken out, horsed to drain and are ready for retanning with chrome.

Preparation of chrome liquor: 10% (B. & C. Mills, Madras) Chrome extract (with 24-25% Cr_2O_3 content) is dissolved in 100% boiling water the previous day to give a liquor of about 33 1/3% basicity. Two thirds of the chrome liquor is made 50% basic by adding the requisite amount of soda ash or caustic soda. The alkali is dissolved in water and is added very slowly to the cooled chrome liquor stirring well all the time. The chrome liquors are left to age overnight.

Retanning: The skins are put into a drum containing 300% water and 1/3 chrome liquor (33 1/3% basic) is added. After 30 minutes drumming, the remaining 2/3 chrome liquor (50% basic) is added in two equal instalments at an interval of 20 minutes. After 3-3½ hrs. drumming, 2% sodium sulfite dissolved in sufficient water is added to the drum in slow feeds over a period of 30 minutes. The goods are drummed for one hour after the addition of sulfite and the pH of the bath is checked. It should be between 3·8 and 4·0. The skins are horsed up over-night. Next morning a piece from the neck portion is cut and its shrinkage temperature determined. It should be not less than 100°C.

Neutralising: The skins are washed in a drum twice with 800% water, allowing 15 minutes for each wash. They are then neutralised with 1% borax, 3% sod. acetate and 400% water in a drum for 40 minutes. The borax-sod. acetate mixture is added in 2 or three instalments in intervals of 10 minutes. After 40 minutes drumming a piece is cut from the neck portion and the pH of the cut edge tested with bromo cresol purple. The pH of the cut edge should be 6 to 7. The neutralised skins are washed

in 800% water for 20 minutes followed by another wash in 400% water at 45°C for 10-15 minutes.

Dyeing and fatliquoring: The skins are put in a drum containing 400% water at 55°C. 4% Ultralan orange G.S. (I.C.I) dye is dissolved in suitable quantity of hot water, strained through a cloth and added through the hollow axle in two portions at an interval of 10 minutes. After 30 minutes drumming, 10% sulfonated fish oil and 1% borax emulsified with hot water is added to the drum in two portions at an interval of 10 minutes (0·5% pine oil may be mixed with sulfonated fish oil to cut down the smell). Drumming is continued for 50-60 minutes after the last addition of fat liquor after which 2% acetic acid diluted with fifteen times its weight of water, is added in 3 portions at intervals of 5 minutes. After the last addition of acid, the drum is run for 15-20 minutes. The skins are taken out, rinsed and piled. Next day they are set and hooked to dry.

With some of the skins, semi-chrome and fat-liquored as above, retannage with basic aluminium sulphate has been carried out.

Retanning with basic aluminium sulphate: The fat liquored leathers are washed in a drum for 15 minutes with 600% water after which they are retanned in a drum with 5% basic aluminium sulphate extract and 100% water in a drum for 10 minutes after which they are set and hooked to dry.

The dried skins are kept in a pile for a minimum period of 3 days. They are then saw dusted for 2-3 hours after which they are staked and dry drummed for 4-5 hours. They are again staked and again dry drummed for 4-5 hours. The goods are removed, aired off, trimmed, buffed on the flesh side and the buffing dust removed.

Finishing :

Season :—

Pigment paste	1 part	
Synthetic resin (Primal B41	5 parts,	1¼ part
Primal S	1 part	
Carnauba wax emulsion 10%	¼ part	
Water	3 parts.	

The skins are given one pad coat of the above season on the grain and dried. They are staked lightly and sprayed with the season to cover. The skins are dried well, staked and are then sprayed with EMG lacquer emulsion and dried.

They are lightly staked, and french chalk is applied on the grain. The skins are cold plated using light pressure after wiping off the chalk with a cloth.

N.B. The percentages given are all based on the crust weight of the raw material.

TECHNICAL SEMINAR

Paste Drying *

BY

S. P. PANDIT

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In the conventional procedure of manufacture of chrome leather, the finishing operations are comparatively tedious because of the elaborate procedures followed for drying and samming. The paste drying process is advantageous in this respect.

This drying process has been in vogue for the last 15 years only. The unit for this process is costly and further, because glass sheets are utilised, damage due to breakage is great. There are certain cheaper types of units available; these are not, however, effective. In the paste drying unit, there is effective control of temperature and humidity. The paste used is made of starch and flour. For the pasting to be quite successful, fatliquor also should be properly controlled. Greater area yield is obtained by this process.

* Summary of the talk given on 9th March, 1959.

TECHNICAL SEMINAR

Studies on the Reactive Groups of Collagen: III. Methylation and Guanidination *

BY

K. THOMAS JOSEPH

Summary

Collagen has been esterified with a number of reagents. Full esterification of collagen was achieved with methanolic HCl, methanol and thionyl chloride and methanol and ethyl chloroformate. A phenomenon accompanying the esterification of collagen with methanol and ethyl chloroformate was an increase in the amino nitrogen content. This has been traced to N-O-Acyl migration in serine and thereonine residues.

* Summary of the talk given on 20-3-1959

CLASSIFIED ABSTRACTS

PROCESSES PRIOR TO TANNING

A PROGRESS REPORT ON THE ENZYME DEPILATION OF CATTLE HIDES. *Theone C. Cordon, W. Windus, I. D. Clarke and J. Naghski, J.A.L.C.A.* **54**, pp. 122-139 (1959). In a survey of some 40 enzyme preparations for hair-loosening activity, several possessing rather marked activity were found. The relation of depilatory action to hydrolytic activity in these active preparations is shown. The conditions for use of one of the most active preparations are given, and some special equipment devised for studying enzyme activity on hides and skins is described.

Result of tests in which whole hides were treated with enzymes and unhaired on conventional unhairing machines are presented, and the problems encountered are discussed.

VEGETABLE TANNING

THE SULFITE EXTRACTION OF SPRUCE BARK. *Anton Blažej and Elena Markušovská (Tech. Univ. Slovakia, Bratislava). Věda a výzkum v průmyslu kožedělném* **3**, 43-52 (1958); *Chem. Abstr.* **52**, 16771 (1958). Chemical analyses of spruce bark (*I*) were made before and after extraction with water or with different amounts of a 1:1 mixture of $NaHSO_3$ and Na_2SO_3. The analysis consisted of a series of extractions beginning with benzene (resins) followed in order by EtOH (sugars, tannins, and 'other compounds'), water at 100° (polyuronides, no tannins), 0·05*N* HCl under reflux for 30 minutes (polyuronides, pentosans, hexosans), and 2% HCl (more pentosans and hexosans). Lignin was determined in the insoluble residue from the last HCl extraction after hydrolysis with 72% H_2SO_4 at 24-6°. Samples of *I* were extracted with H_2O and with 8 different percentages of the sulfite-bisulfite mixture, increasing from 1% of each on the bark weight to 11·5% of each. The extracts were analysed for tannin by the usual procedure. Extractable tannin in the bark increased from 8·8 by H_2O extraction to 17·9% by extraction with the highest concentration of sulfite. However, analyses of the extracted barks

showed that the additional material fixed by hide powder that is extracted by sulfite is not tannin, but consists of polyuronides, hemicelluloses, and a small amount of disaccharides. ANALYSIS OF TANNING BARKS AND WOODS. *Anton Blažej. Ibid.* 119-26. The need for chemical analysis of *I* as a prerequisite to its better utilization is stressed. A sample of *I* was analyzed by the successive extraction method, various constituents being determined in the extracts. Its composition was: H_2O 14·5; resins 3·1; EtOH extract 11·2, including tannin by the filter bell method 7·7; monosaccharides 1·1; oligosaccharides 1·4; and other nontannins 1·0; polygalacturonic acid (Carré-Heynes' method) 0·7 in H_2O extract and 3·1 in 0·05*N* HCl; cellulose (Kúrschner-Hiffer method) 21·2; lignin (König-Komarov method) 25·3; pentosans (Tollens method) 8·2; hexosans 9·5; ash 2·3; N 0·9%.

TANNING EXTRACT FACTORIES FOR SPRUCE BARK. *Ivan Binko* (*Leather & Allied Trades Research Institute, Gottwaldov, Czech.*). *Věda a vyzkum v prumyslu kožedělném* **2**, 13-25 (1957); *Chem. Abstr.* **52**, 16771 (1958). Data are given on current and expected production, economics, and suitable extractors for spruce-bark extract. Extraction at 70-90° is recommended because pectins are extracted at higher temperatures. Sulfite extraction is not recommended. INFLUENCE OF TEMPERATURE AND CHEMICALS ON THE EXTRACTION OF SPRUCE BARK, WITH METHODS FOR THE DETERMINATION OF PECTIC SUBSTANCES AND POLYSACCARIDES IN ITS EXTRACT. *Ivan Binko, Jároslav Kolar, Zdenka Pospícholová, and Ican Ivanic. Ibid.* 77-87 — Extraction of bark from chemically debarked trees has been described. Use of NaOH gives very viscous extracts (*I*) containing pectins (*II*) and polysaccharides (*III*). The following method for determining *II* and *III* is proposed: *I* solution (150 ml) is added to 300 ml. EtOH denatured with Et_2O. The precipitated *II* centrifuged dissolved in H_2O eventually by heating, and saponified cold with 100 ml. 0.1*N* NaOH in 2 hours. The solution is acidified with 50 ml. AcOH and precipitated after 5 minutes with 25 ml. 2*N* $CaCl_2$. The Ca pectate is filtered on tared paper, the filtrate is boiled 5 minutes and filtered through the same paper, and the precipitate washed free from Cl^- and dried at 100-5°. Polygalacturonic acid (*IV*) = (Ca pectate × 176)/195. The combined filtrates are evaporated to dryness. The residue is hydrolyzed 14 hours with HCl under reflux, and hexoses are determined with Fehling solution. Pentoses and pentosans are also determined in the residue by dehydration of xylose to fur-

as the color intensity. The relation between absorption and concentration was investigated in extracts contg. 54·7% of *II*, 59·2% of *III*, 68·8% of *IV* and 70·2% of *V*. The determination of tannins were performed by the Baldraco method. A linear relation between absorption and concn. was proved in the following ranges from $3{\cdot}35 \times 10^{-4}$ to $5{\cdot}03 \times 10^{-3}$ for *I*, from $4{\cdot}13 \times 10^{-4}$ to $4{\cdot}13 \times 10^{-3}$ for *II*, $3{\cdot}63 \times 10^{-4}$ to $5{\cdot}44 \times 10\text{-}3$ for *III*, from $4{\cdot}23 \times 10^{-4}$ to $6{\cdot}34 \times 10^{-3}$ for *IV* and $4{\cdot}30 \times 10^{-4}$ to $4{\cdot}30 \times 10^{-3}$ for *V*. It was concluded that the nature of an extract has an effect on light absorption; the effect of pH is of secondary importance. In the case of *I* the absorption at pH from 8·1 to 9·1 is constant, at pH = 7·6 somewhat increased. The absorption increase caused by change of pH range from 9·1—8·1 to 8·1—7·6 was 2·5 % for *I*. *II* exhibits an identical behaviour at pH from 7·6 to 9·1 whereas at pH = 6·8 absorption decrease was roughly 5 %. *III* characterizes a const. absorption at a range of pH from 6·8 to 9·1 whereas *IV* from 7·6 to 9·1. *V* is characterized by a linear relation between absorption and pH soln. The extracts also contain small amts. of non-tannin substances of the PhOH-like type. The latter content varies with the extracts. The following values were found: 4-8 % for *I*, 2-4 % for *II*, 4-8 % for *III*, 1-3 % for *IV* and 1-3 % for *V*. By using the data of Kurasnov and Zaprometov the distribution of OH groups in different positions was calculated. The following values were found for the location of OH groups as in pyrogallol: 24·8 % for *I*, 28·5 % for *II*, 20·4 % for *III*, 17·8 % for *IV* and 2·5 % for *V*. *V* showed that also a very small amt. (~0·06%) of OH groups had the constitution of pyrocatechol.

OTHER TANNAGES

SYNTHESIS OF A NAPHTHALENE-SULFONIC TANNING AGENT FOR WHITE SKINS. *Ya. P Berkman and A. N. Sergeeva. Nouch, Zapiski L'vov. Politekh. Inst.* 1956, No. 2, 121-6; *Zhur. Khim.* 1957. Abstr. No. 10520. *Chem. Abst.* 52, 16774 (1958). The preparation of a synthetic tanning agent for white skin by the condensation of naphthalene-β-sulfonic acid (*I*) and dihydroxydiphenyl-sulfone (*II*) with CH_2O was investigated. The condensation is carried out in an aqueous medium at 100-120°. The mechanism of the reaction has not been established. Tanning agent specimens were prepd. from pure *I* and tech. *S*, and they contained various amounts of free H_2SO_4; other specimens were prepd. from tech. S and various combinations of *I*, *II*, and CH_2O. The optimum of CH_2O appears to be 0·5 g· mole/mole of *I* and

II. The filling capacity of the tanning agent increases with increasing concn. of *II*, as is shown by an increase in the degree of tannage of the skins from 17 to 59. By changing the ratio of *I* to *II*, tanning agents for different types of skins can be prepd. Skins treated with naphthalenesulfonic tanning agents are characterized by a pure white color which does not show signs of aging after prolonged storage. A faint yellowing of the color is observed when the skins are exposed to sunlight.

PROCESSES AFTER TANNING

THE USE OF FISH OILS FOR FATLIQUORING LEATHER—I. MENHADEN OIL AND COD OIL FATLIQUORS, *Victor Mattei and William T. Roddy, J.A.L.C.A* 54, pp. 12-27 (1959). In an effort to find new uses for menhaden oil in the tanning industry, leather fatliquored with menhaden oil was compared to leather fatliquored with cod oil and neats-foot oil. The last two oils are presently used in the tanning industry for this purpose.

The physical properties of leather fatliquored with menhaden, cod, and neatsfoot oil have been studied in the laboratory and on a pilot-plant scale. With respect to strength properties, no important differences were noted. The leather fatliquored with neatsfoot was the least firm of the three leathers. The firmness properties of the leathers fatliquored with menhaden oil and cod oil were similar. There was no indication that polymerization properties of menhaden oil produced an undesirably hard leather surface.

Compared to leathers fatliquored with menhaden oil or with cod oil, leathers fatliquored with neatsfoot oil did not show yellowing of leather surfaces and showed the least decrease in extractable grease upon aging. Spew formation, an undesirable effect on leather surfaces, was not noticed on any of the leathers.

WASHING AND SEPARATION OF SULFOESTERS IN MANUFACTURE OF FATLIQUORS FOR LEATHER. *Vladimir Pilc* (*Leather & Allied Trades Research Inst., Gottwaldov, Czech*). *Kozarství* 7, 154-7 (1957); *Chem. Abstr.* 52, 16771 (1958). Washing at 35° and maintaining this temperature for 14-16hours of separation is recommended. Example: Fish oil of I value 115 or its mixture with sperm oil 400 are sulfated with H_2SO_4 (93 %) 100 parts at 15-25° for 3 hours. Mixing continues for a further 2-3 hours. The temperature must not rise over 25°. Washing

follows with 500 % of 20 % Na_2SO_4 solution at 23-5°. The temperature rises to 30-4°. The emulsion is left to settle for 14-16 hours at a constant temperature of 35°. Water is drained and sulfoesters are neutralized by NH_3 to pH 6·2-7·0 (10 % emulsion). Sulfation of oxidized paraffins is possible only by this method.

POLYSULFIDE RUBBER TREATMENT FOR GLOVE AND SHOE UPPER LEATHERS, *E. C. Dogliotti, C. W. Mann and J. Barry, J.A.L.C.A*, **54**, pp. 85-100 (1959). A process is described for treating cowhide glove and similar flexible types of leather with liquid polysulfide polymers to produce a high degree of resistance to penetration or absorption of petroleum products, liquid chemicals and water. The polymer is applied to the grain layer only and is heat-cured in the usual drying tunnel to form a protective barrier in the leather without serious detraction from the feel or flexibility of the leather or the ability of the flesh side to absorb perspiration. A small-scale tannery trial is described showing the possibility of plant application without difficulty. The results of a field-wear trial of treated leather gloves are presented.

USE OF AMINO RESINS, IN TANNERIES AND THEIR INFLUENCE ON MOLD GROWTH. *Evžen Pospíšil and Pavel Safařík (Leather & Allied Trades Research Inst., Gottwaldov, Czech.). Kozarstvi* **7**, 93-6 (1957); *Chem. Abstr.* **52**, 16772 (1958). Amino resins (*I*) are condensation products of PhOH, HCHO, and NH_4Cl or $(NH_4)_2SO_4$. When *I* was used with $Al_2(SO_4)_3$ to impregnate leather, heavy growth of mold (*II*) (*Penicillium glaucum* and *Aspergillus niger*) occurred in leather dryers. Tests showed that *I* in small concentration is a N nutrient for *II*; in higher concentration *I* inhibits *II*. The effect of syntans on *II* varies. Phenolic syntans, K_1D, Sn_{25}, and SP are more effective *II* inhibitors than the naphthalenic BNO and Kortan Q_1. Both *I* and $Al_2(SO_4)_3$ react with syntans, liberating OH groups and lessening the *II*-inhibiting action.

DEVELOPMENT OF PIGMENTED CASEIN FINISHES. *Ladislav Blažek (Leather & Allied Trades Research Inst., Gottwaldov., Czech.) Kožařství* **7**, 215-17 (1957); *Chem. Abst.* **52**, 16774 (1958). Plasticizers for casein (*I*) and their influence on quality of *I* finishes have been studied. A sulforicinate (*II*) with 3·9 % org. SO_3 softens *I* well and gives translucent solns. *II* (75-100 %) on dry substances of *I* prevents its fixation by HCHO. Glycerol (*III*) may be added upon 50% of *I*. It does not prevent the fixation of *I* by HCHO. Triglycol (*IV*) is better than *III*, gives translucent solns. and 75-1000 % of *IV* does not prevent the fixation of *I* by HCHO, but the films shrink a little after a 72-hr. heating at 70°. Diglycol is more volatile than *IV* and its films shrink more during heating. The extensibility of good *I* films containing 60-70 % plasticizer is lowered by fixation with HCHO to 18-24 %. The addition of pigments, waxes, etc., lowers extensibility by 30-50 %. New replacement products for *I* have been tested. Luron-binder U without plasticizer gives films with extensibility of 116 and 45% before and after fixation with HCHO resp., "Calfaplast" with 50 % *IV* has extensibility of 60 and 36 %.

TESTING

INFLUENCE OF AMINO RESINS ON THE RESISTANCE OF VEGETABLE TANNED LEATHER TO SWEAT. *Miroslav Mička (Leather & Allied Trades Research Institute, Gottwaldov, Czech.). Kožařství* **7**, 128-30 (1957), *Chem. Abstr.* **52**, 16772 (1958). The effect of artificial perspiration on the shrinkage of vegetable leather retanned with amino resin (*I*) was studied. Vegetable leather insoles, insoles retanned with *I* and neutralised, and retanned with *I* but not neutralized, shrank 8·7, 2·2, and 2·3%, respectively after 35-day exposure to artificial sweat. Corresponding shrink values for insoles worn 4 months were 14·0, 9·2, and 11·5 %. A method for measuring discoloration of socks in contact with insoles is described. A filter paper is sandwiched between a leather disk and a rubber sponge saturated with artificial sweat. A 100-g. weight is applied, and the assembly is stored at 37°. The paper is dried at 50° and its light reflectance is measured by a Lange photocell. Reflectances, in 10^{-9} amp. were: unstained paper 55, papers stained with vegetable leather 30, leather retanned with *I* and neutralised 49, the same not neutralised 44, and black paper 6. Reflectance standards for slight, medium and strong staining are proposed.

THE DETERMINATION OF CHROMIUM IN LEATHER BY MEANS OF COMPLEXON *III*. *Zděnek Hrabal and Jiří Křivinka (Leather & Allied Trades Research Inst., Gottwaldov., Czech.) Kožařství* **7**, 283-4 (1957); *Chem. Abst.* **52**, 16773 (1958). The intensity of the red-violet color of the Cr-complexon III Complex is proportional to the Cr content. The sample should contain approx. 10 mg· Cr. Boil 0·5 g· of leather in 25 ml. HCl and HNO_3 (3 : 1) neutralize by Na_2CO_3 after cooling, and add 10 ml. AcOH and 15 ml. 0·5 *M* complexon III. Boil 10 min., cool, dilute to 250 ml.,

filter on activated C, and measure the color on a Pulfrich photometer. The differences from the standard gravimetric method are — 0·06 to 0·13 % Cr_2O_3 in leather.

SYNTANS FROM DIHYDROXY PHENOLS. I. PAPER CHROMATOGRAPHY OF PYROCATECHOL. *Zdenek Kotásek (Leather & Allied Trades Research Inst., Gottwaldov. Czech), Věda a Výzkum v prumyslu kožedělném* 2, 5-11 (1957); *Chem. Abst.* **52**, 16772 (1958). A novolak (*I*) from pyrocatechol (*II*) has been prepared by dissolving 55 g· *II* in 50 ml. H_2O adding 19 ml. HCHO (40%) and 3 ml. HCl (37%), heating to 50°, and, after 10, min., raising the temperature from 64 to 90° and holding at 90° for 3 hrs. *I* was water soluble. The descending and ascending chromatograms of *I* were studied. Best results were obtained with BuOH-CCl4, which Mráz used for chromatography of dihydroxy phenols. The differences of Rf values of *II* between M. (0·67) and K are explained by different systems of development of chromatograms. K used BuOH saturated with H_2O plus CCl_4 (1 : 9) for 8 hrs. at 20°, dried the chromatogram at 20°, and developed by a 1 % soln. of ammoniated $AgNO_3$ or by a 2% soln. of NH_4 phosphomolybdate. The Rf value of *II* was 0·70 varying from 0·65 to 0·75 and Rf values of components of *I* were 0·60, 0·50, 0·40, and 0·30.

THE EFFECT OF STRETCHING DURING CHROME TANNING ON THE TENSILE STRENGTH AND ELONGATION OF TANNED, AIR-DRIED PROTEIN FIBERS. *A. V. Yudin and M. P. Kotov. Trudy Kiev. Tekhnol. Inst. Legkoi Prom.* 1955 No. 7, 19-26; *Referat Zhur. Khm.*, 1957, Abstr. No. 10091; *Chem. Abst.* **52**, 16773 (1958). The raw fiber obtained from a 40 % soln. of the glutin-gelatin protein fraction containing 10 % triethanolaminooleate was investigated. The molded fiber was kept for 24 hrs. in a saturated soln. of $Al_2(SO_4)_3$ at 20°. The effect of stretching during the chemical fixation of the structure of the raw fiber with basic Cr salts on the fiber tensile strength, elasticity, diam., and the adhesion of the fibers in the oil was investigated. The tanning of the fibers in the free state produces inferior physicomechanical properties. Depending on the amount of stretching applied during the tanning process, it is possible not only to fix the structure of the raw fibers but to obtain an additional orientation of the mol. chains with a corresponding increase in the tensile strength of the fibers. Increasing the tanning time leads to a reduction in the shrinkage of the fiber and in the rate of relaxation.

CHARACTERIZATION OF CARBONYL COMPOUNDS BY PAPER CHROMATOGRAPHY. I. *Takeo Tsukamoto and Sachiko Nishioka (Univ. Kyushu). Yakugaku Zasshi* **78**, 810-12 (1958); *Chem. Abst.* **52**, 16125 (1958). For the qualitative estimation of carbonyl compds., 19 kinds of aliphatic, aromatic, and terpenic carbonyl compds., were converted to 2, 4-dinitrophenylhydrazones and subjected to paper partition chromatography; liquid paraffin used as the stationary phase and MeOH as the mobile phase effected good qual. estn. of aliphatic and terpenic carbonyl compds. Further examns. of solvent systems are necessary for the estn. of aromatic carbonyl compds. by this method.

MICROTITRATION OF PROTEINS. *A. C. Maehly. Bull. Schweiz-Akad. med. Wiss.* **11**, 433-62 (1955). *Excerpta Med.* 10, Sect. II, Abstr. No. 33 (1957); *Chem. Abst.* **52**, 16455 (1958). The applicability and errors of acid base titration of proteins are discussed. A new micromethod is described for the titration of protein. Results obtained with this method on horse-radish peroxidase compare favourably with those of Theorell with a conventional method. Quant. estns. of ionizable groups are possible with as little as 2 mg. protein.

STUDIES OF THE QUALITY OF LEATHER MADE FROM CALFSKINS OF CURRENT PACKING HOUSE PRACTICES, *Robert B. Combs, William T. Roddy and Jospeh Naghski, J.A.L.C.A.* **54**, pp. 62-84 (1959). Studies have been made to determine the quality of calfskin leather representative of two current packing house practices. In one system the skin remains on the carcass when it is placed in the cooler, to prevent shrinkage in weight of the carcass, and eventually the skin is removed in the cooler (cold pull). In the other system skinning is done immediately after slaughter (regular flay). Two lots of 120 calfskins, one of each practice, were analyzed and evaluated in the cure and as finished leather. No differences were found that could be attributed to the different practices or that indicated that one method was superior to the other as to leather quality. However, some interesting aspects of the relation of the strength of the raw stock to that of the finished leather have been noted, and such data are presented.

SEMIMICRO TECHNIQUES FOR EVALUATION OF LEATHER FINISHES. *Peter R. Buechler, Ernest R. Jones, and Stanley Chmielewski, J.A.L.C.A.* **54**, pp. 140-160. (1959). An apparatus has been developed for following the rate of penetration of

liquids into porous surfaces by photographic semimicro techniques. The rates of penetration of various leather finish formulations have been determined accurately by this procedure. Studies can be made on single drops of finish formulations. Variations in rate of penetration in various portions of the hide have been studied. In addition, the wettability of the leather by the finish and the final height of the finish on the leather surface can be easily determined from the same series of measurements.

By the use of the microscope and some simple histological staining techniques, the final depth of penetration of the pigment and the binder portions of finishes were determined. The final depth of penetration of a finish does not necessarily coincide with its rate of penetration. The penetration characteristics of pigment and binder are very dissimilar.

The apparatus for measuring penetration rate was described. The practical significance of the findings was discussed.

THE VISCOSITY OF CONCENTRATED GELATIN SOLUTIONS AT ELEVATED TEMPERATURE. *A. S. Fokin. Trudy Kiev. Tekhnol. Inst. Legkoĭ Prom.* 1955, No. 7, 33-43; *Referat. Zhur. Khim.,* 1957, Abstr. No. 10083; *Chem. Abst.* **52** 16775 (1958). Gelatin solns. containing ~15 % protein at 40° have a structural viscosity dependent on the space lattice formed by the anisodiametric protein mols. The energy of formation of that lattice apparently is not very large. Samples of commercial gelatin and proteins extracted from leather wastes were investigated. It was established that solns. of proteins extd. by neutralization from chrome-tanning wastes contg. 0·57 % Cr_2O_3 can be used in the production of artificial fibers. The viscosity of the protein soln. is dependent on the heating time, the temp., and the concentration of the protein. The addn. of HCHO increases the viscosity of the protein soln. The addn. of upto 0·8 % HCHO (calculated on the wt. of the protein) leads the formation of a gel which does not melt at 100°.

THEORIES

STUDIES ON ZIRCONIUM TANNAGE. THE MECHANISM OF THE TANNAGE. *T. S. Ranganathan & R. Reed. J.S.L.T.C.* **42**, 351 (1958). The present studies appear to show that zirconium tannage, under the conditions used in these experiments, cannot be regarded as being similar to chrome tannage with regard

to the mechanism. From the knowledge available till now it appears that though carboxyl groups are not involved, the amino groups play some part in the fixation of zirconium to hide protein. The zirconium may be attached by mechanisms not involving the amino groups, since deaminated hide powder is still capable of fixing appreciable amounts of zirconium. In this respect zirconium tannage would seem to resemble more closely vegetable tannage in its mechanism.

BIOSYNTHESIS OF COLLAGEN. III. DIRECT ACTION OF ASCORBIC ACID ON HYDROXYPROLINE AND COLLAGEN FORMATION IN SUBCUTANEOUS POLYVINYL SPONGE IMPLANTS IN GUINEA PIGS. *Bernard S. Gould* (*Massachusetts Inst. of Technol., Cambridge*). *J. Biol. Chem.* **232**, 637-49 (1958); *Chem. Abst.* **52**, 16449 (1958). Collagen biosynthesis as detd. by hydroxyproline synthesis in subcutaneously implanted polyvinyl sponges was studied in normal, scorbutic, and ascorbic acid-treated guinea pigs. Hydroxyproline formation in such a system under various conditions is analogous to hydroxyproline formation in granulation tissue. A direct specific effect of ascorbic acid in collagen biosynthesis *in vivo* was demonstrated. Administration of relatively small doses of Na L-ascorbate into implanted sponges in previously ascorbic acid-depleted guinea pigs resulted in rapid hydroxyproline synthesis in the treated sponge with little or no synthesis in a control sponge in the same animal. When ascorbic acid was administered by mouth at the same time that it was introduced directly into the site of collagen formation, an additive effect was observed. The direct action of ascorbic acid appears to be specific for substances of known antiscorbutic activity since dihydroxymaleic acid, glucoascorbic acid, and isoascorbic acid are inactive whereas L-ascorbic acid and L-dehydroascorbic acid are active. Rapid collagen biosynthesis such as that involved in tissue repair may be directly mediated by ascorbic acid, in contradistinction to collagen formation in tissue culture, which appears to be independent of ascorbic acid; the possibility is suggested of more than a single biosynthetic pathway.

INTERACTION BETWEEN PROTEINS AND COMPLEX SALTS. *E. A. Bauman. Sbornic Nauch. Trudov Vinnitsk Gosudarst. Med. Inst.* **8**, 92-106 (1957); *Referat. Zhur. Khim., Biol. Khim,* 1958, Abstr. No. 9626; *Chem. Abst.* **52**, 16436 (1958). A study was made of the effect of anionic complexes on pure proteins.. The anionic complexes were: trioxalatochromiate, hexo-

cyanoferroate, hexocyanoferriate, Na complex of trivalent Fe in tartaric acid, trioxaloferriate and tetrachloroplatoate. The purified proteins were egg albumin, horse serum albumin, bovine serum albumin (*I*), insulin, bovine α- and β-globulins, γ-globulin, gliadin, and gelatin. A study was also made of the effect of the cationic complex hexamine cobaltichloriate on *I*. Detns. were made of the degree of binding of the complexes by the proteins based on the content of the corresponding metals; the stability of the complexes was judged by the ease of extraction of the protein with acids and salts. Treatment of proteins with anionic salts reduced the no. of basic, carboxylic, and mercapto groups in cases of weak or unstable inner sphere complexes as in the case of trioxaloferriate; such innersphere interaction did not increase the stability of protein-complex union to any noteworthy degree.

THE THERMAL SHRINKAGE OF COLLAGEN IN SOLUTIONS OF ELECTROLYTES. *W. G. Crewther and L. M. Dowling* (*Wool Textile Research Labs. Melbourne*). *J. Phys. Chem.* **62**, 678-84 (1958) *Chem. Abst.*; **52**, 16435 (1958). The rate of shrinkage of kangaroo-tail tendon in 0·1 *M* buffer solns. at 50 and 60° is minimal at a pH of about 9. At pH values greater than 5 the rate of shrinkage is increased by incorporating salts in the buffer solns., the relative effect of different salts being related to the position of their constituent ions in the lyotropic series. At pH values below 5 the presence of salts in the buffer solns. usually causes a decrease in rate of shrinkage. At pH 2·0 the rate of shrinkage first increases to a max. as the concn. of salt is increased, then decreases as the conc. of salt is further increased. At pH values sufficiently high to cause shrinkage of collagen in buffer solns. at a rate comparable to that at pH 2·0, the rate of shrinkage increases with salt conc. over the whole conc. range. It was suggested that there is preferential absorption of the anion of the salt at the interface between the protein and the soln. The kinetics of shrinkage of the tendon are consistent with the assumption that the units of structure of the collagen are converted to the denatured form in a random manner by a 1st-order reaction but that the denatured units are initially prevented from contracting completely by the rigidity of the residual native collagen.

METALLIC ACID ESTERS. I. CHROMIC ESTERS OF PRIMARY AND SECONDARY ALCOHOLS. *Hans-Ludwig Krauss. Z. Naturforsch.* **13b**, 199-201 (1958); *Chem. Abst.* **52**, 15984

(1958). Esters were prepared by the reaction of CrO_3 with dil. solns. of the alcohol in an inert solvent. The presence of CrO_4 groups was confirmed by infrared spectra and the diamagnetism of the product. Kinetics of the spontaneous decompn. of the esters was studied spectrophotometrically. The decompn. is 1st-order, the half-life increasing with the chain length of the alc. Branched-chain and secondary alcs. have a longer half-life than do primary alcs. with the same no. of carbons. At room temp. the reduction of Cr(VI) to Cr(IV) is accompanied by the formation of an equiv. amt. of aldehyde. At higher temps. the aldehyde is oxidized further. A ppt. is formed with a compn. corresponding to H_2CrO_3. A reaction mechanism is postulated.

BYE-PRODUCTS

UTILIZATION OF LEATHER-INDUSTRY WASTES. *Cyril Halámek, Michael Radil, and Jaroslav Lačňok* (*Leather & Allied Trades Research Inst., Gottwaldov., Czech.*) *Kožařství* **7**, 275-8 *Chem. Abst.* **52**, 16774 (1958). The most economical use for large quantities of sole leather cuttings (*I*) is for fuel; its calorific value equals soft coal. The best use is defiberization and incorporation in plastic leather. Alkali-hydrolyzed *I* can be used for mordanting wool. Uses of *I* for fertilizer after acid hydrolysis, and detannization with NH_3 followed by recovery of tannin and use of the protein for feed-stuffs after acidification, are not economically sound. Dry distillation of *I* has been tried. Urbánek (unpublished) has isolated amino acids and peptones from *I*. Other proposed uses are for case-hardening steel, polishing metals, and production of activated C. Cr leather shavings and cuttings (*II*) are used mostly for making plastic leather. *II* can be used for making a medium-quality glue. A feedstuff is produced commercially from *II* by acid hydrolysis; pressure hydrolysis will be more economical. The N of the feedstuff is 43·1% protein and 39·5% nonprotein; the feedstuff contains only 0·04 Cr_2O_3. It has been used successfully to provide 5% of the total protein fed to pigs replacing fish meal. Split fleshings are used to make artificial casings and with other fleshings, for making gelatin and glue.

PATENTS

CONDENSATION PRODUCTS OF CARBOHYDRATES, SULFUROUS ACID AND ITS DERIVATIVE, PHENOL AND FORMALDEHYDE. *Richard Alles.* **U.S. 2,837,489** *June* 3, 1958; *Chem. Abst.* **52**, 15107 (1958). The reaction of the materials

named in the title in an aqueous alkaline solution free of organic compounds, having sulfonic groups gives compounds useful as nonhydrolyzable tannins and preservatives. Thus, 400 parts of a 50% aqueous solution of D-glucose was added to a solution of 104 parts $NaHSO_3$ in 130 parts water at 50°. Separately, 409·6 parts cresol and PhOH (6:4 ratio) were mixed with 10 parts NaOH in 15 parts water and 400 parts 30% aqueous HCHO was added. The mixture was refluxed for 1 hour at 70° and 5 hours more at 80°, giving an oily condensate. This was added to the glucose-bisulfite solution and stirred at 90° for 1·5-2 hours, until a diluted sample, acidified with AcOH, gave a completely clear solution. The reaction product, acidified with AcOH to pH 3·5—4·5, was a tanning agent. When 7 moles of cresol-PhOH mixture is thus allowed to react, hydroxyaryl groups replace all the primary OH groups on the carbohydrate. Subsequent treatment with 6 moles more replaces all the OH groups with hydroxyaryl groups. Other examples describe use of sucrose and fructose as carbo-hydrate and O-chlorophenol and 4, 6-dinitro-2, 5-dichlorophenol as the hydroxyaryl constituents. The products are said to have many other uses, e.g., in the textile industry and in the preparation of disinfectants and pharmaceuticals.

TANNING MATERIALS FROM SULFITE WASTE LIQUOR AND LIGNIN EXTRACTS. *Hermann Babel,* **Ger. 930,341,** *July* 14, 1955. *Addn. to* **Ger. 898,350**; *Chem. Abst.* **52,** 15107 (1958). In the main patent, a procedure for the production of tanning agents is described in which the sulfite waste liquor and the lignin extracts are mixed with aqueous solutions containing ferrocyanide and ferricyanide ions and then exposed to light. Separation into 2 layers also takes place in the absence of light. If the original matter originates from deciduous wood and if tap water is used, a blue colouring may result. This is avoided by making all the solutions alkaline. Thus, to 200 g. sulfite waste liquor diluted with 200 cc. water (pH 4·5) a solution of 4 g. Na_2CO_3 and 40 g. $K_4(Fe(CN)_6)$ in 400 cc. water (pH 10) was added in a dark room with shaking. The mixture was kept for 2 weeks in a brown bottle wrapped in lightproof paper. Then, 350 cc. of a brown liquor was siphoned from the top. The precipitate settled on the bottom was washed several times with 250 cc. 2% aqueous Na_2CO_3 until the solution and precipitate were colourless. For tanning, a solution of 3 kg. of the residue from the 1st 3 portions of liquor in 24 l. water was acidified with 270 cc. concentrated HCO_2H to pH 4·5 and the precipitate filtered off. The precipitate can also

be used as a tanning agent by acidifying the aqueous solution with concentrated HCO_2H to pH 6·5.

GENERAL

TESTING THE SCRUBBING OF CHROMIUM COMPOUNDS FROM VENTILATION AIR BY MEANS OF STEAMING AND WASHING. *N. P. Anashikina and I. M. Satonin-Bukharev. Voprosy Gigieny Truda. Professional. Patol i Toksikol v. Prom. Sverdlovsk. Oblash. Sverdlovsk. Shornik* 1955, 204-8; *Referat. Zhur. Khim* 1957, *Abstr. No.* 7025. *Chem. Abst.* **52,** 16661 (1958). The tests were conducted in a bichromate manufg. plant, a coke filter being used, at filtration rates of 275-1250 cu. m. of filtered air/hr. After a preliminary steaming and scrubbing with water the air was passed consecutively through 2 or 4 frames, 600 x 554 x 80 mm., filled with granulated coke of 10-50 mm. particle size. With an initial content of 0·12-0·73 mg. CrO_3/cu. m. of treated air, filter resistance of 4·7-25·6 mm. water column, steam consumption of 0·03-0·16 kg./kg. of air, and water expenditure of 1·29-4·37 kg./kg., a 68·4-94·9% coeff. of purification was attained. The tests showed that it is possible to achieve residual concns. of Cr compds. in the air that are within the standard specifications for air to be recirculated (0·03 mg./cu. m) but this involves steam expenditures exceeding by several times those required for preheating the same vol. of outside air. To decrease pollution of the air discharged to the atm. an economic and efficient scrubbing of the ventilation air with water without steaming is recommended.

NOTES & NEWS

SOLE LEATHER DEVELOPMENTS

It is significant that whereas prior to 1955 requests for testing new sole leathers were rare (though there was keen interest in Wear Index determinations of conventional tannages), there has been a steady flow since that date. The most outstanding result, for durability, has been given by a flexible full-chrome (Durability Ratio 2·1, which compares with an average of between 0·4 and 0·5 for vegetable bends). This type of leather is not sufficiently waterproof to be used on outdoor footwear (though the wear trial was, in fact, on boys' school shoes in autumn weather). For several possible reasons, wax-impregnated full-chromes have not given such good results for wear, though they are definitely better than normal vegetable bends (one waxed full-chrome gave a D.R. of 1·2, other about 0·6). These well-established leathers are, nevertheless, still probably the most suitable when waterproofness and good wear are the essentials. As they are also resistant to heat damage and iron rot (the latter is important when iron grindery of any kind is used) they have much to commend them. At least one such leather has normal flexibility. Waxed chrome retans (with high chrome contents) have also given an average D.R. of about 0·6. (There are a few flexible retans with high chrome contents: only one has been tested for wear and this, too, gave a D.R. of 0·6. These leathers are not waterproof. The majority of flexible chrome retans have a low chrome content, under 1%: the D.R.'s of those which have been wear tested are in the same range as vegetable bends. They tend to be more flexible but less waterproof than the latter).

Impregnated vegetable leathers cannot be discussed as a class since the type and amount of impregnant can vary so widely, and it is impossible for the shoe manufacturer to know what he can expect from a particular product unless the results of a scientifically conducted wear trial are available. One such leather, now available commercially, has shown a worthwhile improvement over ordinary bends. An interesting result is that the flanks and the butt gave very similar D.R.'s. As leather soles which are

complained about often come from the flanks (sometimes one of a pair shows up badly compared with its fellow from the butt) this levelling-up may prove to be a valuable feature.

Perhaps the best all-round results in the tests of sole leathers have been given by a small piece of French Zirconium leather. It was reasonably flexible, attractive in colour and appearance, well above average in the laboratory water penetration test and had a D.R. of 1·9. But, of course, tests on one small sample may be very misleading.

The D.R. values given are all for the butt or middle region.

—*Satra Bulletin*, 8, No. 1, 6 (1958).

W. GERMAN LEATHER OUT PUT IN 1958

Production by the West German Leather industry as a whole amounted to 77,684 tons during 1958 compared with 81,375 tons in 1957. It was 6,085 tons in December 1958, compared with 6,336 tons in November and 6,361 tons in December, 1957.

Leather shoe imports in the first 11 months of 1958 were over 2,160 tons, worth 69,078,000 D-marks. Exports of Leather shoes during that period amounted to 1,268 tons worth D-marks 27,104,000.

—*Leather Traders' Rev.*: 18-2-1959.

HOW UPPER LEATHERS IMPORTS (INTO U.K.) FINISHED IN 1958

Full chrome calf and hide upper leather imports in 1958 amounted to 44,358,621 sq.ft. compared with 42,766,045 sq.ft. in 1957. The following were the leading exporters to U.K. with 1957 figures in brackets:

Box and willow calf: France, 3738 million sqr.ft. (3,402 million sq.ft.); India 3,089 million sq. ft. (3061 million sq.ft.). Box and willow sides: Eire 7,724 million sq.ft. (6,458 million sq.ft.); Australia 2,630 million sq.ft. (2,2203 million sq.ft.) Hide upper leather: Australia 12,097 million sq. ft. (10,607 million sq. ft.); India, 2,589 million sq. ft. (3,426 million sq. ft.).

Australia's total exports to the U.K. of full chrome calf and hide upper leathers amounted to approximately 27·75% of the over all total imports and India's to nearly 13·5%.

Imports of glace and suede kid and patent leather were lower than in 1957. But W. Germany remained the leading exporter of all three of these items, and India was again second.

Leath. Trades' Rev.: 18-2-1959.

Japanese tanners find new outlet for by-products

Hide fleshings which could not be utilised as material in gelatin factory, are converted into cattle and poultry feed through cultivation of 'Rhizopus fungi' by Koji fermentation process. In this process hide scrap is mixed with starch residues, wheat bran etc., fermented by the Oriental Koji system and Rhizopus fungi stock culture is inoculated.

Rhizopus koji-feed (Hinomaru feed) is claimed to be a useful nutriment added to other feeds for raising cattle and poultry. Chief effects claimed are: saving of animal protein feed; promotion of growth and egg production; uniform growth of poultry; increase in hatchability; improvement of meat quality; and good physiological effect on poultry.

— *Leath. Trades' Rev.*: 8-2-1959.

Bringing new life to an old indusrty in Nigeria

Long before white men set foot in West Africa, large quantities of "Morocco" leather are known to have been exported across the Sahara from what is now known as Nigeria. These tanned goatskins, mostly dyed a "red" colour, were much sought after for their hard-wearing properties and resistance to age as well as for the pleasing natural "grain" of the skins. This art of tanning has been handed down through scores of generations.

During the past 40 years or so, two or three trading companies have bought and exported tanned goat skins and tanned sheep skins from the native tanners. The crust tanned products are dyed and finished for shoe upper leather, upholstery leather, gas meter bellows, book-binding etc.

The Nigerian goatskin is endowed with a finer grain than its Indian counter-part; the skin of the true sokoto 'Red' goat, makes the best kid in the world.

A tannery has been built at Kano in Northern Nigeria for turning out products of uniform quality for the foreign dressers,

without departing very much from the basic native methods, so as to preserve the inherent qualities of the moroccan leather. The local traditional vegetable tanning medium, *Bagaruwa*, the fruit pod of a variety of acacia, which has a very high tannin content is used in this tannery.

—*Leath. Trades' Rev.*: 18-2-1959.

New spray against warble fly attack

H. E. Helman & Co. (Insecticides) Ltd. announce the introduction of a new chemical—warble-mite—to prevent warble fly attack. The repellant action of this spray, is claimed to eliminate irritation and panic during seasons of prevalency of warble. One spray per year is said to ensure immunity from warble fly attack, and it is recommended that treatment be carried out between January & March.

The method of application is to spray the back and flanks of each animal from an approximate distance of three feet.

—*Leath. Trades' Rev.*: 18-2-1959.

London or Madras?

Agitation is kept alive by a certain section of the E.I. tanned skins industry—and by no means an important section—that the E.I. tanned skins auctions, which have been held in London over the past one hundred years, should be taken out of this country and set up in Madras.

Last year, the president of the Southern India Hide and Skin Merchants' Association, presented a petition to the India Minister for Commerce and Industries, containing the most astonishing allegations of malpractice at the London auctions and praying the Government of India to take steps for removal of auctions from London to Madras. The allegations were not only promptly refuted by London brokers and Director of the British Leather Federation but also denied by more responsible interests in India.

The Madras Minister for Industries says that the Government was considering the question of removing the hides and skins market from London to Madras; he also admitted that the opinion was divided.

One of India's biggest exporters of E.I. tanned skins, said, in London, recently, that fresh steps in this direction were quite un-

necessary as they already had the equivalent of a market in Periamet which was patronised by all the principal exporters from Madras for the execution of orders received from the U.K. and continental countries.

Informed opinion in this country (U.K.) is that when the Government of India does arrive at a decision it is likely to favour a continuance of the present trading methods rather than to change a system, that on the whole has, worked well for many years.

—*Leath. Trades' Rev.*: 11-2-1959.

Curing sheepskins with antiseptic and salt

In an experiment on curing sheepskins, using antiseptics and salt very promising results had been obtained with sodium silicofluoride. This was stated at a meeting of the sheep pelt tanners' Research Committee, B.L.M.R.A. It was decided to test this on a larger scale.

—*Leath. Trades' Rev.*: 11-2-1959.

How wattle industry came to Natal

Modern wattle industry in Natal earns over £ 5 million a year through exports alone. An article on U.K. export opportunities in Natal in the Board of Trade Journal describes how an English immigrant in the middle of the 19th century brought a match-box full of seeds from the black wattle trees of Tasmania.

—*Leath. Trades' Rev.*: 4-2-1959.

Firm Market for Goat at E.I. Tanned Skins Sales

On Tuesday, last week, at the resumed auctions of E.I. tanned goat-skins, the market was firm at December prices to 6*d*. per lb. above, and sometimes a little more, the maximum advances being obtained for light-weights.

Heavies and extra heavies found a weak market and were occasionally unchanged, but in most cases a concession of 3*d*. per lb. had to be made to effect sales.

There was a firm finish on Wednesday, with no further change in the market quotations.

About 160,000 skins were sold.

Auctions of tanned E.I. sheepskins were commenced on Thursday, the categories comprising: 363,000 sheepskins against 407,000 in December and 571,000 in October.

There was a good attendance of home trade buyers. The market was dull with little active competition.

New shipments realised December prices to 6*d*. per lb. below on average for all descriptions.

Old stock, where sold, changed hands on the same basis, but the bulk of it was limited far above the market and consequently remained in stock.

When the auctions concluded on Friday the market closed at the previous day's quotation, but rejection classes were occasionally dearer.

About 180,000 skins were sold.

—*Leath. Trades' Rev.*

ASSOCIATION OF TECHNOLOGISTS: UNIVERSITY OF MADRAS, LEATHER BRANCH

A meeting of the Association of Technologists, University of Madras, Leather Technology Branch, was held at the Central Leather Technology Branch, was held at the Central Leather Research Institute on the 6th February, 1959. Mr. Nazir Ahmed, M.A., Secretary, Southern India Wool and Goat Hair Exporters' Association, spoke on Leather Industry and export of wool and goat hair.

Dr. Y. Nayudamma, Director, Central Leather Research Institute, presided on the occasion.

The valedictory address of the association of Leather Technologists University of Madras Leather Branch was delivered at the Central Leather Research Institute on Monday, the 9th March, 1959, by Sri S. P. Pandit, Director, Western India Tanneries, Bombay. Dr. Y. Nayudamma presided on the occasion. In the valedictory address Shri Pandit spoke about the paste drying of leathers.

FOUNTAIN PEN INK, PERMANENT

A Draft Indian Standard Issued

The Indian Standards Institution has drafted a specification for Fountain Pen Ink, Permanent [Doc: CDC 13 (969)], which

prescribes the requirements and the methods of sampling and tests for fountain pen ink for permanent records.

It may be recalled that a Draft Indian Standard Specification for Ferro-Gallo Tannate Fountain Pen Ink, Colour as Required, Doc: CDC 13 (938) was issued for wide circulation in October 1958. That draft covers fountain pen inks, required for producing semi-permanent records which are not likely to be required after about ten years. For records which are expected to be of more permanent nature, ink of higher iron content is necessary. With that idea in view and on the suggestion of the National Archives of India, the Indian Standards Institution has issued this draft standard, which is proposed to be ultimately merged with Doc: CDC 13 (938). This document covers fountain pen inks containing 0·2 per cent iron (as Fe), so writings, written with ink conforming to this specification, are expected to last for about 50 years, under normal conditions.

Copies of the draft standard are available, from the offices of the Indian Standards Institution, located at New Delhi, Bombay, Calcutta and Madras.

SPECIFICATION FOR RUBBER HOSES

Two Indian Standards Issued

The Indian Standards Institution has just published the following two Indian Standards pertaining to rubber hoses:

(1) Specification for Braided Air Hose, Light Duty (IS: 912-1958). This standard prescribes the requirements and the methods of test for braided air hose, light duty, with cotton or rayon braided reinforcement for compressed air and pneumatic tools.

(2) Specification for Braided Water Hose, High Pressure (IS: 913-1958). This standard prescribes the requirements and the methods of test for water hose, high pressure, with cotton or rayon braided reinforcement used for car washing and spraying of mild solutions of insecticides.

Both the standards are published in English and are priced at Rs. 1·50 per copy. Copies of the standards are available from the offices of the Indian Standards Institution, located at New Delhi, Bombay, Madras and Calcutta.

18-LITRE SQUARE TINS

An Indian Standard Specification is Issued

The Union Parliament having adopted the Standards of Weights and Measures Act, 1956, the Government of India is now concerned with expediting the introduction of the metric system of weights and measures in various branches of commerce and industry. At the instance of the Standing Metric Committee of the Government of India, the Indian Standards Institution has taken up the formulation of the Indian Standards on metal containers in metric system.

As a basic approach to the problem, the Institution is formulating standards on metal containers on the basis of their respective capacities by volume and not by weight of the materials to be packed therein.

The Indian Standard Specification for 18-Litre Square Tins (IS: 916-1958) which has just been issued by the Institution, covers the requirements for 18-litre square tins manufactured from tinplate. The 18-Litre tin is based on the 4-gallon tin, which is in extensive use in India, judging from the fact that the tonnage of tinplate consumed for 4-gallon tin represents nearly 65 percent of the total tinplate used in India. The 4-gallon tin is used for packing various types of commodities, such as kerosene oil, vegetable oils, vanaspati, insecticides and chemicals, cashewnuts, food products, etc. Consequently, the 4-gallon tins, as at present made in India, are used for packing various commodities exported all over the world; and, as such, represent an important item of foreign exchange earning. The method of manufacturing these tin containers varies enormously; the large-scale organized factories employing completely automatic plants, while simple techniques employing manual labour are also used by a large number of fabricators. It is expected that the standard will assist the industry the production of square tins of quality, and in switching over to the metric system.

Copies of the standard, published in English and priced at Rs. 1·50 each, are available from the offices of the Indian Standards Institution, located at New Delhi, Bombay, Madras and Calcutta.

SPECIFICATIONS FOR BRAIDED HOSES

Two Indian Standards Issued

The Indian Standards Institution has issued the following two Specifications for Braided Hoses:

(i) Indian Standard Specification for Braided Air Hose, Heavy Duty (IS: 911-1958). This standard prescribes the requirements and the methods of test for air hose, heavy duty, with cotton or rayon braided reinforcement for pneumatic tools, rock drill and mining.

(ii) Indian Standard Specification for Braided Water Hose, Low Pressure (IS: 914-1958). This standard prescribes the requirements and the methods of test for water delivery hose with cotton or rayon braided reinforcement, suitable for working pressures up to 7·0 kg per sq cm (or 100 lb per sq in.).

The standards lay-down general requirements such as construction; dimension & tolerances; and tensile strength & elongation of lining & cover of the respective types of hoses; while the methods of tests concern accelerated ageing test and hydraulic test.

Copies of the standards, published in English and priced at Rs. 1·50 each, are available from the offices of the Indian Standards Institution, located at New Delhi, Bombay, Calcutta and Madras.

C. L. R. I. NEWS

PUBLIC ACCOUNTS COMMITTEE VISITS C.L.R.I.

Profesor N. G. Ranga and Sri S. Venkataraman of the Public Accounts Committee visited the Central Leather Research Institute on 31-3-'59. They were very much impressed with the research work in progress at the Institute. They felt happy to find that the Institute fitted with modern equipment, offered training facilities to students coming from other countries also.

Dr. Y. Nayudamma, Director, received the members and showed them round the tannery, work shop, pilot plants and laboratories.

Sri K. V. Karunakara Menon, Administrative Officer, Central Fuel Research Institute, Jealgora, has been transferred to the Central Leather Research Institute with effect from 22nd Feb. 1959.

Shri A. Ganesan, Senior Scientific Officer, has been nominated as a member of the Leather Belting Sub-Committee EDC 42-2, of the Indian Standards Institution, New Delhi.

Dr. Y. Nayudamma, Director, attended a meeting of the Research Committee of the Khadi and Village Industries Commission, which was held at Wardha on 16th March, 1959.

Dr. S. K. Barat, Assistant Director, attended a meeting of the Sub-Committee for Vegetable Tanning Materials of the panel for leather and leather goods industry (Ministry of Industries and Commerce) held at Nagpur on 12th March, '59.

Sri A. Ganesan, Senior Scientific Officer, attended a meeting of the Extension Advisory Committee of the Council of Scientific & Industrial Research held at New Delhi, on 14th March, 1959.

A meeting of the Executive Council of the Central Leather Research Institute was held on 26th March, 1959.

A process for manufacture of up-holstery leather from E. I. tanned kips by semi-alum tannage is being demonstrated to tanners at the premises of M|s. I.E.C. (Private) Ltd., Calcutta, by the Central Leather Research Institute Extension Service team consisting of Sri R. Selvarangan and Shri G. N. Hore.

The Central Leather Research Institute is participating in the Red Cross Society Centenary Exhibition organised at Madras.

Sri A. Ganesan, Senior Scientific Officer, has left on an Extension Service Survey tour of some North Indian provinces.

Change in practical demonstration programme:

The demonstration of the process of manufacture of Kattai and Banwar Leathers will be held from 15th May to 25th June.

An improved process for manufacture of chrome upper leather will be demonstrated from 28th May.

Editor Y. Nayudamma. Published by N. Subramanian, on behalf of the Central Leather Research Institute, Adyar, Madras-20. Printed by G. Srinivasachari, B.A., at The G. S. Press, 21, Narasingapuram Street, Mount Road, Madras-2.

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