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Bulletin of the

Central Leather Research Institute

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Announcing the publication of:

C. L. R. I. BULLETIN I

Adapted Processes for:

Manufacture of Box Sides

A number of German Processes for the Manufacture of shoe upper leather Box Sides have been investigated with a view to adapt them for Indian raw materials and climatic conditions. These have been modified and adapted for producing leather of good quality. Details of the processes have been published in the above bulletin.

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or

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Announcing the publication of

C. L. R. I. BULLETIN No. 3

"Manufacture of Roller Skins"

Three different processes for the manufacture of Roller Skins from East India sheep skins and from chrome tanned calf developed by the Central Leather Research Institute have been published.

Copies of the Bulletin can be had from:

The Assistant Director-in-charge,

CENTRAL LEATHER RESEARCH INSTITUTE,

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OBITUARY

We deeply regret to announce the sudden demise of Prof. B. M. Das, M.A. (Cal.), M.Sc. (Leeds), Director, Central Leather Research Institute, Madras and Founder-Editor of this Journal at 11.05 P.M. on Wednesday, the 5th September 1956 due to Coronary Thrombosis.

C. L. R. I. MOURNS THE DEATH OF ITS FIRST DIRECTOR

In the death of Prof. B. M. Das, the Leather Industry in general and C.L.R.I. in particular has sustained a great loss. The association of Prof. Das with Leather Industry dates back to the time he worked in Leeds University under Prof. Procter and Prof. Edmund Stiasny. From then onwards, he had been throughout closely associated with this industry in some capacity or other right till his death. The Bengal Tanning Institute and the Central Leather Research Institute are ample proof of his untiring zeal in the cause of Indian Leather Industry. His one great ambition was to work without respite in this field as long as he could and this he realised through his death in harness.

Prof. Das was characterised by a genial temperament and great forbearance. He was ever ready to help his students and associates in any manner he could. His words carried so much weight that his suggestions were continually sought in choosing personnel for posts in the various branches of this Industry. Though of advanced age, he would be always seen working tirelessly, taking visitors round the Institute and explaining to them in his characteristic style.

The least one could do in his memory would be to continue his efforts for the uplift of this industry and make India occupy a prominent position in the map of Leather Industry.

His memories will be enshrined in the C.L.R.I. which is the best edifice we can have and it will be our efforts to make this Journal live up to the high ideals for which he stood in his life time.—*Ed. Board.*

Prof. Das suddenly took ill with a heart attack in the early hours of Wednesday, the 5th September, 1956. He was taken for treatment to the General Hospital, Madras where he passed away at 11-05 p.m. Next morning his body was brought to his residence at Gandhinagar. His Excellency Shri Sri Prakasa, Governor of Madras, Dr. A. Lakshmanaswamy Mudaliar, Vice-Chancellor of the University of Madras and Chairman, Executive Council of the Central Leather Research Institute, several officials and prominent members of the Leather Industry and Trade were among those who called at his residence to pay their last respects. On its way to the crematorium, the cortege touched the Central

Leather Research Institute, Adyar, the Alagappa Chettiar College of Technology, Guindy and the premises of the Bengal Association in T'Nagar and of the Southern India Skin and Hide Merchants' Association, Periamet, where wreaths were placed on behalf of the various institutions and organisations. At the Choolai Crematorium, Shri P. M. Sundaram, Secretary of the Council of Scientific and Industrial Research, New Delhi who paid his last respects to the departed Director, laid wreaths on behalf of the Vice-President, C.S.I.R. and Director-General of Scientific and Industrial Research. The cremation took place at 4-30 p.m. Prof. Das is survived by his wife, three sons and three daughters.

Earlier, a condolence meeting was held under the Chairmanship of Dr. A. Lakshmanaswamy Mudaliar. Dr. Mudaliar who described the late Prof. Das as a loving personality, recalled that Prof. Das came to Madras in 1951 after the sudden and tragic demise of Dr. A. L. Sundara Rao, his predecessor in office and said he had made this Institute equal to any other international institute ever established. He added that in his loss we had sustained a great disaster.

The following resolution was then read and passed in the usual manner.

> "This meeting of the Staff, students and employees of the Central Leather Research Institute bemoans the loss sustained by the Institute at the sudden demise of their beloved Director, Prof. B. M. Das and conveys to the members of the bereaved family their sincere condolence at the irreperable loss sustained by them.
>
> This meeting also conveys through the Chairman of the Executive Council the sincere condolences of the Executive Council and of the Council of Scientific and Industrial Research to the bereaved family."

As a mark of respect to the departed soul, the Central Leather Research Institute and the Alagappa Chettiar College of Technology remained closed for the day (6th September, 1956).

At a special meeting of the members of the Southern India Skin and Hide Merchants' Association held on the 6th September, 1956, the following resolution was passed unanimously.

> " This meeting of the members of the Southern India Skin and Hide Merchants' Association, Madras-3 held at 2-30 p.m. on Thursday, the 6th September, 1956 with the President,

Janab Merit Hajee Mohamed Ismail Sahib in the chair, learns with deepest regret the sad news of the sudden demise last night of Sri B. M. Das, Director, Central Leather Research Institute, Madras, and resolves to place on record the services rendered by him in the cause of the development of modern research and technique in the Tanning Industry and to offer the deep sympathy and condolences of the members of the Association to the members of the bereaved family."

MEMOIR

The Indian tanning and Leather Industry is orphaned by the sudden demise of Prof. Biraj Mohan Das. No figure looms larger in its history as that of Prof. Das whose achievements signalize the greatness and value of a life time devoted to its service. It is a matter of profound regret that he passed away at this time when the country is on the threshold of vast changes in the field of Industry and technology. His sage counsel and abounding enthusiasm will be sorely needed and sadly missed.

Born in the year 1887 in the sleepy little town of Faridpore in East Bengal, Biraj Mohan Das showed early promise for intellectual attainments. After finishing his schooling by the turn of the century, Biraj Mohan came down to Calcutta and got himself admitted at the Presidency College. Nurtured by a congenial atmosphere of learning under Acharya Sir P. C. Roy, his passion for science found true and harmonius expression in his every day experiments and after a distinguished record of scholarship, he passed his M.A. examination in Chemistry of the Calcutta University in 1907, standing first among the successful candidates. Struck by Biraj Mohan's profound love for experimental work, Acharya Roy took him to the Bengal Chemical and Pharmaceutical Works. There followed a period of applied research which at the end resulted in the marketing of the first 'India made' commercial sulphuric acid in the face of keen competition from abroad. During these formative years of his career Biraj Mohan came in close personal contact of Acharya P. C. Roy who in no small measure was instrumental in directing the interests of the young chemist to the development of indigenous industries. Opportunity presented itself, Biraj Mohan was awarded the Guru Prasanna Ghosh Scholarship by the University of Calcutta for advanced training abroad in some branch of technology. Faced with a choice, Biraj Mohan went in for Leather. It was a moment of great decision, a decision which marked him out for a career, not considered to be very covetable for educated youngmen of those days. But Biraj Mohan never regretted this decision and from

that time onwards his was a life of single minded devotion to the cause of leather science and technology in India.

In Leeds, Biraj Mohan became a student of Prof. Procter who was at that time holding the Chair of Leather Industries in the University. He worked with Dr. Edmund Stiasny (Later Professor Stiasny) on the reactions involved in the second bath of the two bath process of chrome tanning. These pioneering investigations made a significant contribution to our knowledge of the chemistry of chrome tanning. Leeds made a deep and abiding impression on him and the so called 'Leeds tradition' manifested itself so often in his later works. After obtaining his M.Sc. from Leeds in 1911, he left for the Continent with a view to rounding up his theoretical training with some practical work in factories and tanneries. For the next two years he worked with M/s. Farbenfabriken Bayer and its subsidiaries in Germany followed by a year's work in a big commercial tannery in Milan, Italy before returning home in 1914.

On his return, he became the Manager of M/s. National Tannery Co. Ltd., Calcutta, a position he held with conspicuous ability and distinction for 24 years. His association with the National Tannery marked the beginning of his active participation in the welfare of the Indian Tanning and Leather Industry which continued with unabated zeal and fidelity till his end. He was instrumental in introducing, for the first time, the commercial chrome tanning in India and was mainly responsible for placing the Indian Tanning Industry as a whole, on a more scientific basis.

As a man of great practical sanity of mind, Sree Das foresaw the need for a Technical Institute for training leather technologists in India, for manning its growing tanning Industry. His dream saw its fulfilment in the establishment of the Bengal Tanning Institute whose stewardship he was called upon to assume in 1919. Born with a heritage of ability, Sree Das found ample scope to build up this Institute as the foremost of its kind in Asia. The tenure of his office as the Superintendent of the Bengal Tanning Institute from 1919 to 1948 was suffused with his personality and as one so prolific in the production of ideas he was undoubtedly the supreme architect of the present set up of technological training in India in this particular branch of the Industry. His was the service much sought after by the Federal, provincial and state governments and in due recognition of this he was awarded the title of 'Rai Bahadur' and the Silver Jubilee Medal. In 1944 he became the Chairman of the Leather and Leather Goods Industries panel of the Government of India and in this capacity he

rendered yeoman's service in connection with the post-war development of these industries. In 1946, at the instance of the then Government of India, he proceeded to Germany as a Technical Investigator under the British Intelligence Objective Sub-Committee to study the technique of German Tanning Industry. The Government of West Bengal also gave him an assignment to study the techniques of the Leather Industry in the U.K. and the U.S.A. which he carried out during the year 1946-47. On his return, he submitted several comprehensive technical Reports which were published by the Government and later made available to the trade. Besides these reports, he was the author of a large number of bulletins and research papers embracing a wide range of subjects on the Chemistry and Technology of leather manufacture. His well known publication 'Hand Book of Tanning' has almost become a classic and has already passed through three editions. Since a classified bibliography of his lectures and papers will be published elsewhere in due course, no further reference to these may be necessary at this stage.

From 1948-51 he held the office of the Industrial Advisor to the Government of West Bengal and was responsible for implementing the development schemes of the Government for the reorganization of the Tanning and Leather industry in the State on modern scientific lines. In September 1951 his services were requisitioned by the Council of Scientific and Industrial Research, Government of India, as the Officer on Special Duty at the Central Leather Research Institute, Madras. In January 1953, he was appointed its first Director and he continued in this capacity till his end. In him the man of action and the man of ideas were combined on the grand scale and the Institute is richer to-day for his being the Director.

Sree Das was the Hony. Professor of Leather Technology and Chairman of the Faculty of Technology, University of Madras from 1954 onwards. He was also the Chairman of the Leather Research Committee of the Government of India, Leather Sectional Committee of the Indian Standards Institution, the Indian Sectional Committee of the International Society of Leather Trades Chemists and the President of the Leather Technologists Association (India). Prof. Das was a man of varied interests and wide human sympathies and his sphere of activity was not confined within the limits of his professional interests alone. He was one of the Senior most active members of the Rotary Club having served as its President and District Governor in Calcutta. Besides, he was associated with very many other philanthropic

organizations of the city which to-day mourn the loss of their sincere patron.

Prof. Das was a friend, mentor and philosopher to his students who are scattered all over India, Pakistan, Burma and Ceylon. Many of them to-day will miss his affectionate letters and no doubt will feel a sense of personal sorrow.

The memory of Prof. Das will be kept alive in the memory of our men of Science and letters and his message will find an echo in the hearts of his colleagues and co-workers who will carry on the work he has bequeathed to them. Thus best shall we pay our homage to the departed soul.

S. K. BARAT.

SPECTROPHOTOMETRIC STUDIES: Part V:

Differential Titration of Phenolic Groups of Vegetable tanning materials by Photometric technique:

Y. NAYUDAMMA, (MISS) A. NAGASIRONMANI & D. RAMASWAMY

SUMMARY

The photometric titration technique in u.v. region has been applied with success to the study of vegetable tanning materials. The phenolic hydroxy groups of the tanstuffs could be differentially titrated due to their differences in ionisation constants. Based on the data obtained a classification of the tanning materials has been attempted and the probable part played during tannage by the individual groups explained.

The application of ultraviolet spectrophotometry to the study of vegetable tanning materials has yielded some valuable results. Qualitative data were obtained[1,2] for the conjugated and non-conjugated phenolic hydroxyl contents of the various indigenous tanstuffs by the differential ultraviolet spectrophotometric technique. Since the absorption spectra give a measure of free, partly hindered and hindered hydroxyl groups of the polyphenolic materials, it would be desirable to get some quantitative data, differentiating these different hydroxyl groups of tannins. Such data will give an insight into the constitution of tannins and to measure the extent to which hydrogen bonding may take place which, in turn, may throw light on the mechanism of vegetable tanning.

In the course of the photometric titration of weak acids contained in the vegetable tanliquors,[3] it was observed that tanliquors contained polyphenolic bodies, that are fairly acidic. Coggeshall *et.al.*[4] have suggested the ultraviolet absorption spectra of polyphenols are influenced by the activation of the hydroxyl groups and by the magnitude of steric hindrance offered by other substituted groups on the ionization of the phenolic group. Since the vegetable tanning materials are polyphenolic and the hydroxyl groups exist in different states of activation, the phenolic groups may conveniently be differentiated by the differences in their acidities. The factors contributing to the differences in acidity of these phenolic groups are: (i) the activation of the phenolic groups by their position in the benzene ring, (ii) the activation by other electron donating groups and (iii) the steric hindrance

due to the presence of a large alkyl or other groups in one or both the O-positions of the phenolic hydroxyl group.

The photometric titration technique offers itself as a valuable tool for differentiation of these acidic phenolic groups in tanning materials. The results obtained in such a study of a wide variety of foreign and indigenous vegetable tanning extracts, viz., mimosa, quebracho, cutch, gambier, chestnut, sumach, myrobalan, Divi-divi, white-valem, Terminalia arjuna, mangrove, Cassia marginata, avaram, Dhawa and Hopea parviflora are reported in this paper.

Experimental:

The experimental procedure followed is the same as that followed and described previously[3] for the photometric titration of weak acids in vegetable tanliquors. Commercial or specially prepared tannin solid or powdered extracts were used. The concentration of the tannin extract was 4-16 g./litre and 5 cc. of this solution was titrated with N/20 standard NaOH. The alkali added to tan solution each time was 0.05—0.1 cc; the mixture diluted to 100-150 times with distilled water free from CO_2 and dissolved oxygen and the differential absorbance values measured in 1 cm. matched silica cells against a blank tannin solution of the same strength to which no alkali was added. The measurements were made at the wave-length where maxima appeared for the particular tanning material, due to the addition of sodium hydroxide. The addition of the alkali to tanliquor was continued till there was no or negligible increase in the absorbance values. The differential absorbance readings were plotted against the amount of alkali (in cc.) added.

Data and Discussion:

An attempt is made here to distinguish the phenolic groups of tanning materials by their variation in dissociation constants. It is to be stated, at the outset, that the results reported in this paper are exploratory in nature and it is not possible at this stage to assert beyond doubt their accuracy. Much work needs to be carried out with pure components of the various tanning extracts before characterising the phenolic groups and their dissociation constants.

The discussion of the results is restricted to the non-conjugated phenolic groups since only those wave-lengths where these groups ionise have been taken into consideration for experimental work. The photometric titration curves (ml. alkali added vs. differential absorbance value plots) are given in Figs. 1-4, for a

Fig: 1

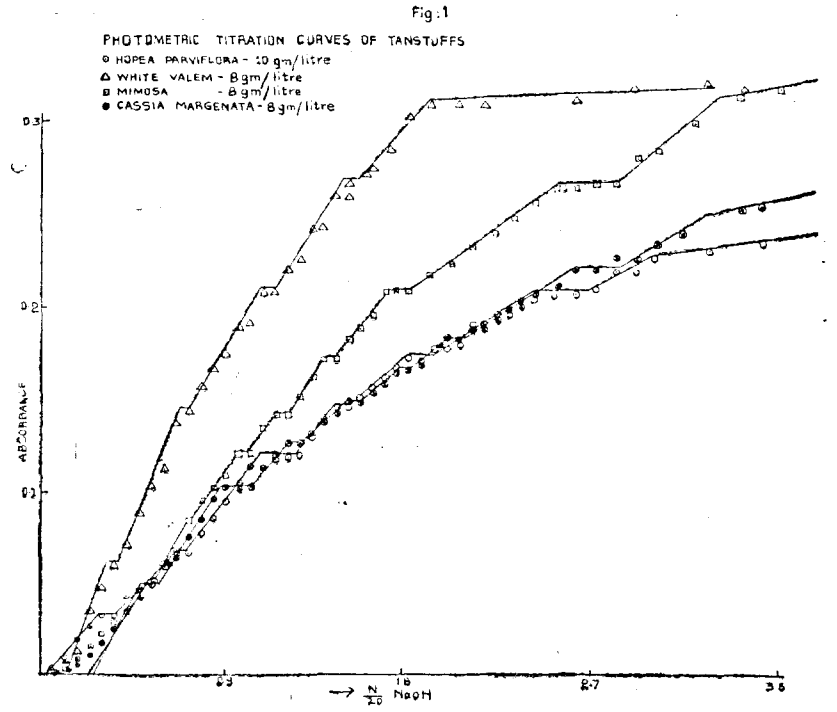


Fig: 2

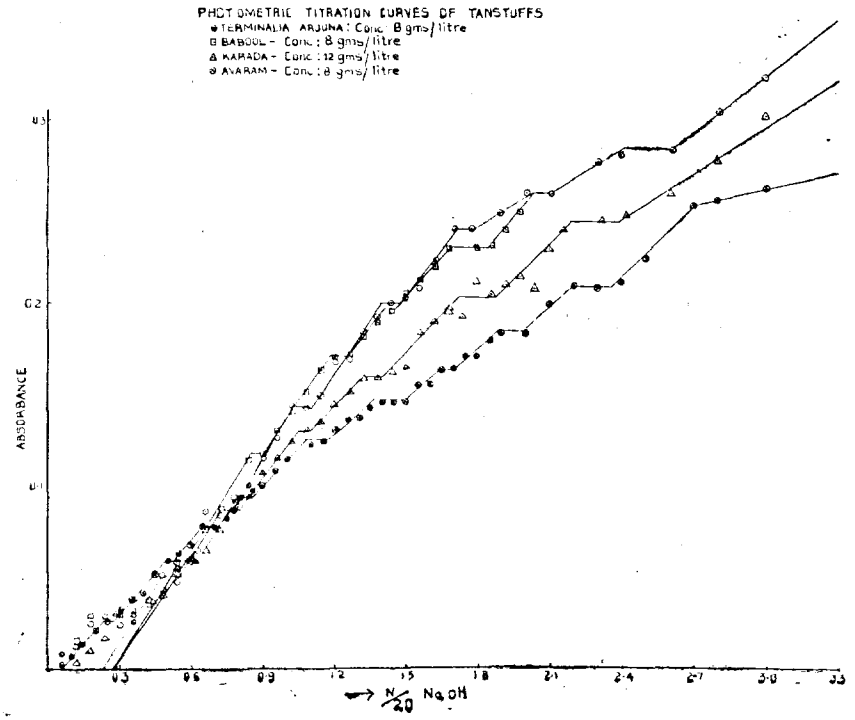


Fig: 3

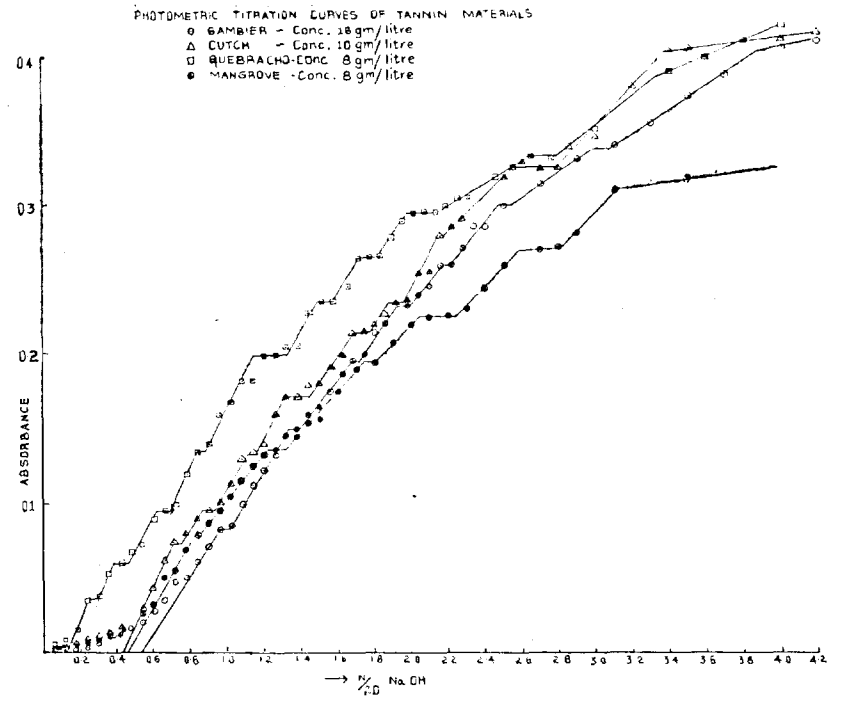
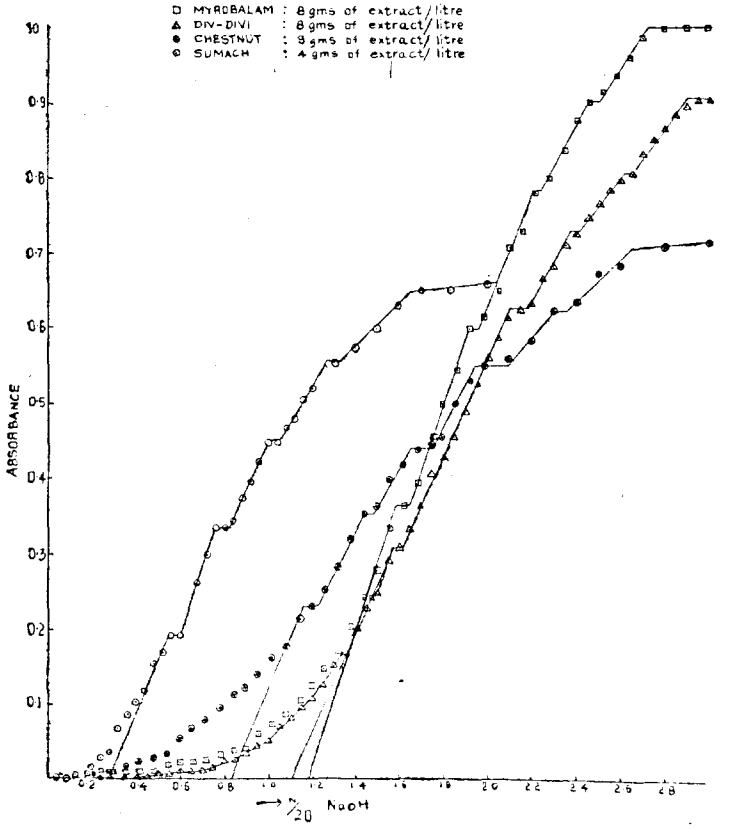


Fig: 4

PHOTOMETRIC TITRATION CURVES FOR PYROGALLOL TANSTUFFS



number of vegetable tanning extracts. Instead of drawing smooth curves joining several ⌣-type curves, the curves were drawn in steps by means of extrapolation, so as to clearly indicate the breaks in the curves. The photometric titration was carried out to such an extent that there was no further increase in the absorbance value with the addition of sodium hydroxide. But in some cases, such a constancy of absorbance values could not be obtained, possibly due to the nature of constituents present in the tanning materials or the limitation of this technique using water as solvent as water interferes with ionisation at high pH values.

The changes in the trends of the curves are due to the different extents of ionisation of the phenolic bodies in alkaline medium. Taking the different breaks in the curves into consideration, the m.eq. of alkali required to titrate individual phenolic -OH groups and the pH values at which these phenolic -OH groups are titrated for various tanning extracts corresponding to 250 gr. of the extract were determined and recorded in Table I.

It is seen that as the free acids present in the tannin extracts get titrated first, there is no increase in the absorbance values. There is an increase in the absorbance values only as the phenol is converted into phenolate ion. The phenol which is most acidic (i.e.) whose pK value is low will be titrated first followed by the -OH groups whose pK values are greater and greater. In the titration of very weak acids such as phenols, it is possible that before one phenol is completely titrated, the second phenol may also get titrated partially. It is for this reason, the curve is drawn in steps by means of extrapolation.

From Figs. 1-4 and Table I, it is observed that apart from free acids, the tanning extracts contain at least 6-8 varyingly ionisable phenolic groups. The titration of the phenolic -OH groups appears to be complete at a pH around 10.0-10.5 where a flattening of the curve occurs. With Terminalia arjuna, babul and karada, such a flattening in the curve did not occur and their values may have to be taken with caution. Babul and White-valem barks contain only 6 different ionisable phenolic -OH groups, whereas Gambier and Quebracho contain 9 and Wattle and Cutch 8 such groups. The rest of them vary from 6-8.

Amongst the pyrogallol tanstuffs, it appears that the phenolic -OH groups are more acidic in nature and get readily titrated even at a pH 9.0. The number of differently ionisable -OH groups are also small: Myrob. 5, Chestnut 6, Sumach 4 and Divi-divi 7.

TABLE I.

Extract	Free acid content in m.eq./ 250g.	pH of neutn.	Phenolic hydroxyl content expressed as m.eq./250 gr. of the extract and their pHs.																	
			I phe-nol	pH	II phe-nol	pH	III phe-nol	pH	IV phe-nol	pH	V phe-nol	pH	VI phe-nol	pH	VII phe-nol	pH	VIII phe-nol	pH	IX phe-nol	pH
Mimosa	84	7.0	72	7.8	69	8.1	75	8.35	56	8.5	75	8.7	131	9.0	250	9.8	250	10.0		
Avaram	16	6.4	63	7.1	125	7.6	103	8.4	94	8.9	131	9.25	125	9.6	172	9.9				
Cassia marginata	75	7.0	113	8.2	89	8.7	95	9.1	94	9.4	75	9.6	75	9.9	197	10.15				
Hopea parviflora	10	5.7	75	7.4	50	8.0	100	8.6	105	9.0	95	9.3	130	9.6	180	9.95				
White-valem	34	7.0	50	7.85	80	8.3	51	8.5	51	8.7	102	9.4	100	10.0						
Terminalia arjuna	75	6.4	75	7.3	75	7.65	113	8.0	100	8.2	103	8.5	166	8.85	219	9.3				
Cutch	118	6.8	53	8.0	48	8.4	53	8.9	58	9.1	93	9.33	135	9.6	75	9.8	233	10.3		
Gambier	71	6.6	41	7.5	38	7.85	60	8.23	56	8.5	34	8.7	38	8.8	44	8.9	63	9.0	177	9.8
Mangrove	147	7.65	113	8.45	122	8.95	163	9.5	97	9.7	172	10.05	155	10.3						
Karada	92	6.4	69	7.4	44	7.8	71	8.15	69	8.4	117	8.8	165	9.4						
Babul	84	6.8	84	7.65	97	8.3	103	8.95	75	9.3	84	9.7	109	10.5						
Quebracho	38	6.5	38	7.3	44	7.9	69	8.25	81	8.6	94	8.85	103	9.1	66	9.3	85	9.5	237	9.9
Myrobalan	375	6.0	119	7.4	106	7.9	91	8.3	78	8.7	91	9.1								
Chestnut	216	6.0	108	6.7	78	8.0	62	8.6	78	9.1	100	9.6	111	10.0						
Sumach	188	6.0	163	7.5	125	8.0	139	8.9	169	9.0										
Divi-divi	357	5.85	191	6.8	44	7.0	66	7.4	103	7.8	75	8.15	72	8.3	116	8.9				

A further careful perusal of the curves reveals that the slope of the curves is reduced considerably and the curves tend to flatten, in the regions where greater amounts of alkali are added and where much weaker type of phenols gets titrated. In other words, there is a perceptible reduction in the slopes of the titration curves for the phenolic groups with high pK values. It would be of interest to differentiate the phenolic -OH groups based on this gradual reduction in slope of the titration curves.

The values for tan θ (slope of the titration curve) are recorded in Table II given below :

TABLE II

Extract	Concn. g./l.	Slopes for the individual phenolic groups - value for tan θ									
		1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th
Mimosa	8	2.14	1.84	1.46	1.43	1.60	1.28	0.71	0.87		
Cassia marginata	8	1.66	1.54	1.32	1.30	0.87	0.64	0.70	0.65		
White-valem	8	2.90	2.48	1.66	1.63	1.11					
Hopea parviflora	10	1.17	1.07	1.33	1.30	0.84	0.65	0.58			
Babul	8	1.51	1.48	1.33	1.17	1.15	1.14				
Terminalia arjuna	8	1.54	1.51	1.48	1.43	1.40	0.84	0.78	0.81		
Karada	12	1.60	1.57	1.38	1.04	1.02	1.00	0.62			
Avaram	8	1.19	1.17	1.13	1.07	1.05	0.93	0.87	0.85	0.84	0.81
Quebracho	8	2.05	2.15	2.01	1.96	1.77	1.64	1.48	0.61	0.73	
Cutch	10	2.25	1.73	1.70	1.80	1.46	1.43	1.73	1.02	1.00	1.11
Gambier	16	1.60	1.70	1.43	1.46	1.26	1.24	0.70	0.71		
Mangrove	8	1.88	1.33	1.19	1.05	1.04	1.02				
Sumach	4	2.48	3.01	2.3	1.6	1.03					
Chestnut	9	2.61	2.41	1.96	1.73	1.88	1.24	0.95			
Myrobalan	8	3.08	2.99	2.75	1.96	1.60					
Divi-divi	8	2.90	2.41	2.19	1.80	1.24					

From Table II, it is seen that the values for tan θ vary from 3.0 to 0.58. For any one titration curve, the values gradually decrease which is only expected on the basis that the readily ionisable -OH groups get titrated earlier at low pH values with a steep slope and the less readily and difficulty ionisable -OH groups get titrated gradually at higher pH values with a gradual decrease in the slope, the titration curve tending to be flat.

The values for the tan θ are very high for pyrogallol tanstuffs (> 1.25) evidently containing mostly the readily ionisable type of phenols, whereas in case of Avaram, the tan θ values are > 1.25 containing only less readily or difficultly ionisable -OH groups. It is probably for this reason, avaram tends to be a mellow tannin. For other tanstuffs, tan θ values vary.

An extension of this concept leads to a broad classification of the differently ionisable phenolic groups and thereby to the classification of the tanstuffs. Taking the range of phenolic -OH groups titrated where the tan θ value (slope) is varied by 1.0 (i.e.), (i) tan θ = 3 − 2.0, (ii) tan θ = 2.0 − 1.0, (iii) tan θ = < 1.0, the m.eq. of OH for 250 gr. of extract are calculated and recorded in Table III given below :

TABLE III :

No.	Extract	Total -O H		Slope Tan θ 3 - 2·0		Slope Tan θ 2 - 1·0		Slope Tan θ <1·0	
				Easily ionisable		Less readily ionisable		Difficultly ionisable	
				-OH	% to total 5/4 × 100	-OH	% to total 7/4 × 100	-OH	% to total 9/4 × 100
1	2	3		4	5	6	7	8	9	10
1.	Myrob	8	g/l	485	316	65.2	169	34.8	—	—
2.	Divi-divi		„	567	304	53.7	263	46.3	—	—
3.	Sumach	4	„	736	425	57.7	311	42.3	—	—
4.	Chestnut	9	„	537	186	34.6	240	44.7	111	20.7
5.	Cutch	10	„	742	53	7.4	689	92.6	—	—
6.	Whitevalem	8	„	434	130	29.9	304	70.1	—	—
7.	Avaram	8	„	829	—	—	376	38.1	513	61.8
8.	Cassia marginata	8	„	935	—	—	391	41.8	544	58.2
9.	Hopea parviflora	10	„	739	—	—	351	47.5	388	52.5
10.	Terminalia Arjuna	8	„	866	—	—	459	53.0	407	47.0
11.	Gambier	16	„	535	—	—	314	58.7	211	41.3
12.	Karada	12	„	566	—	—	394	70.0	169	30.0
13.	Mangrove	8	„	822	—	—	822	100.0	—	—
14.	Babul	8	„	552	—	—	552	100.0	—	—
15.	Quebracho	8	„	998	326	32.7	254	25.4	418	41.9
16.	Mimosa	8	„	978	72	7.4	406	41.6	500	51.0

For making a comparative study, it is assumed the phenolic -OH for whose titration slopes are 3.0 − 2.0 are readily ionisable ;

between 2.0 – 1.0 less readily ionisable and < 1.0 difficultly ionisable types. From a consideration of Table III, some very interesting observations may be made :

1. The total phenolic -OH content for 250 g. extract varies from 998 to 434, m.eq. the highest value being 998 for Quebracho and the lowest for White-valem 434. The order for total phenolic -OH is :

Quebracho (998) Mimosa (978) Cassia marginata (935) Mangrove (882) Avaram (829) Cutch (742) Hopea (739) Sumach (736) Divi-divi (567) ; Chestnut (537) Gambier (535) Myrob (485) White Valem (434).

The values for Babul, Karada and Terminalia arjuna have not been considered as the flattening in the curve was not obtained. Therefore, correct assessment of total phenolic -OH is made difficult. From these data it is clear that it is not the total amount of -OH present that really counts but probably, the different types of phenols and the ratio of such different types to the total that matters.

A sub-division of the total phenols brings out some very interesting results.

(*a*) The pyrogallol tanstuffs like myrobalan, Divi-divi and Sumach contain only the readily ionisable and less readily ionisable type and *not* the difficultly ionisable types of phenols. The readily ionisable -OH groups vary from 50-65% of the total and the less readily ionisable groups account for the rest (35-50%). Chestnut appears to be an exception to this group, though it is of pyrogallol type in that it contains about 20% of the difficultly ionisable type phenols also. It is feared that chestnut extract taken up for analysis which is a commercial product may be a blend.

Though apparently coming in the same category as myrobalan, Cutch and White-valem differ greatly from the myrob. class. These tanstuffs also do not contain any difficultly ionisable type of phenols, but the readily ionisable once are also present only to a small extent (7.4% of the total in case of Cutch and 30% in case of White-valem as compared to 53-65% in case of myrob. class). Cutch differs from White-valem itself in that, it contains still smaller fraction of readily ionisable type phenols (7.4% of the total as compared to 30% of White-valem). Actually this Cutch extract appears to have been blended with lignosulphonic acid which might account for the readily ionisable type. As it

contains 93% less readily ionisable type phenols, it is more akin to Mangrove than to White-valem which is found to be true in practice.

(*b*) As contrasted to the above acidic type tanstuffs, Avaram, Cassia marginata, Hopea parviflora, Terminalia arjuna, Gambier, & Karada form a separate class in that they contain only the less readily ionisable and difficultly ionisable type phenols and not even a trace of the readily ionisable type. Even amongst this group, a further interesting observation can be made. Amongst this group, Avaram contains the maximum amount of difficultly ionisable phenols (61.8%), followed by Cassia marginata (58.2%). In fact, Cassia marginata and Avaram compare very closely in that the less readily ionisable phenols are 38.1% & 41.8% respectively and the difficultly ionisable phenols account for 58.2% and 52.5%. No wonder Cassia marginata bark could substitute avaram bark. That such is the case has been conclusively proved by practical tanning experiments. This category of tanstuffs may be further grouped in the order of increasing % of less readily ionisable phenols. The order is as follows (See Table) :

Avaram, Cassia marginata, Hopea parviflora, Terminalia arjuna, Gambier and Karada. Avaram has 38% less readily ionisable phenols and 62% difficultly ionisable phenols whereas in case of Gambier, it is 59% and 30% respectively and in case of Karada it is 70% and 30% respectively.

3. Another category of tanstuffs appear to be Mangrove and Babul. These tanstuffs contain only the middle class, namely, the less readily ionisable type of phenols and not even a trace of other types, i.e., readily ionisable and difficultly ionisable types.

4. Yet another category is Quebracho and Mimosa extract. These tanstuffs contain all the three types of phenolic groups. Quebracho differs from wattle in that it contains a greater percentage of readily ionisable phenols and a lower percentage of less readily ionisable type of phenols. Mimosa extract contains 51% of difficultly ionisable type, 42% less readily ionisable and 7% of readily ionisable type.

5. From the above discussion, one is led to speculate further. It is quite likely that the difficultly ionisable type phenols will account for the mellowness 62% highest in avaram followed by Cassia marginata 58%, Hopea 52%, and Mimosa 51%. The less readily ionisable and/or the difficultly ionisable may contribute

to the penetration and the yield of leather in tanning, whereas the readily ionisable type which are acidic may help fixation of tannin. If the percentage of readily ionisable type of phenols is too great, the fixation is too rapid, thereby retarding further penetration, resulting in non-uniform fixation of tannin and low yield. Such is the case with pyrogallol tanstuffs where the readily ionisable phenols are over 50% of the total.

From this account, the reasons for the superiority of Mimosa extract over others is obvious. It contains a fairly good amount of less readily and difficultly ionisable phenols which will regulate the penetration and yield, together with a small amount of readily ionisable type which will regulate gradual fixation of tannin.

From these data, it is also possible to work out substitute for any given materials. Such an attempt is being made to confirm such an idea.

6. One is tempted to speculate further. It is quite likely that these phenols varying in the ionisation may account for the (*a*) fixed, (*b*) loosely bound and (*c*) free tannins in leathers.

7. One more aspect of speculative interest is regarding the hydrogen bonding of vegetable tannins. The variation in the slope of titration curves is probably caused by the differences in the energy and entropy of acid dissociation of phenolic bodies as suggested by Minegishi and Nagakura.[5] If the slope is greatest, the energy involved in electron donating capacity of the phenolic nuclei to the medium (water in this case) is very great. One of the favourable conditions of hydrogen bonding being the energy difference, the slope may bear some relationship to the hydrogen bonding. Since the modern concept of the mechanism of vegetable tanning implies multi-hydrogen bonding, it would be of interest to assess the part played by the activated and readily ionisable phenolic groups whose slope is greatest compared to the less readily and difficultly ionisable phenols.

8. At this time, it is necessary to point out that these discussions, though interesting and adds somewhat to our knowledge of the complex nature of tannins, are very purely highly speculative. Such an approach, therefore, needs confirmation but may, however, lead others to expand upon. But one thing appears to be fairly certain, i.e., the tanstuffs vary in the total as well as individual phenolic groups and the ratios of differently ionisable groups to the total has a great significance.

Determination of the phenolic -OH :

It is possible to calculate from the total m.eqs. of phenolic hydroxyl corresponding to 250 g. of the extract the % phenolic hydroxyl knowing the equivalent weight of OH, i.e., 17. The % phenolic hydroxyl calculated in this manner are recorded in Table IV.

Table IV :

	Extract	% phenolic hydroxyl by the present method.	% phenolic hydroxyl by the previous method.
1.	Mimosa	6.7	7.2
2.	Avaram	5.5	—
3.	Cassia marginata	6.4	6.5
4.	Hopea parviflora	5.0	6.3
5.	Whitevalem	3.0	—
6.	Terminalia arjuna	5.2	10.8
7.	Cutch	5.0	6.3
8.	Gambier	3.8	—
9.	Mangrove	5.6	—
10.	Quebracho	5.9	12.0
11.	Myrobalan	3.3	4.0
12.	Divi-divi	3.8	3.3
13.	Divi-divi	3.8	4.2
14.	Sumach	3.7	—

The values thus obtained are compared with the values obtained earlier[3] for phenolic hydroxyl by adopting Goldschmidt's technique of taking known model compounds. It is seen that the values agree very well. In case of pyrogallol tanstuffs, the current values lie between 3.3–3.8 while the previous values were 3.8–4.2 by the other technique. This close agreement shows that all the titratable non-conjugated phenolic hydroxyl groups have been obtained. Mimosa and its indigenous known substitutes like Cassia marginata, Hopea etc. lie between 5.0 and 6.7 whereas they are between 6.3 and 7.2 by the other technique. The maximum deviation occurs only in case of Hopea i.e., 5.0 and 6.3. The same difference in value is observed in case of Cutch also. With Quebracho and Terminalia arjuna, the values obtained by the present technique are only 5.9 and 5.2 whereas 12.8 and 10.8 are the values which have been reported previously.

The discrepancy for these two extracts has been stressed in the previous paper itself. The present values seem to be more reasonable. Wherever there is discrepancy between the values by the two techniques, it can be traced to any one of the following reasons: (1) that the model compound taken in the previous technique is not representative of the tannin material under investigation, (2) that the phenolic groups have not been completely titrated by the present technique, (3) that the buffer added in the previous method had formed some complex with the phenolic group of the tanning material.

However, the general agreement in a majority of instances shows the soundness of both the techniques for finding out the % phenolic hydroxyl content.

Conclusions :

The following conclusions were drawn as a result of the study of photometric titration of tanning materials.

The tanning materials contain anywhere from 6-10 different types of phenolic -OH groups varying widely in their ionisation capacity. The tan θ values for the decreasing slopes of the titration curve for each tan extract were calculated. Based on these values for varying slopes, the phenols were classified into three groups, namely, (*a*) readily ionisable, (*b*) less readily ionisable and (*c*) difficultly ionisable phenols; the readily ionisable groups getting titrated earlier with high values for tan θ of the slope. Percentage of each of these groups to the total phenolic -OH groups was also calculated. From the above data, the following classification is made :

Tanstuffs containing a & b — (1) Myrob, Divi-divi and Sumach.
(2) Whitevalem, cutch.
„ b & c — Avaram, Hopea, Cassia marginata, Terminalia arjuna, Gambier and Karada.
„ b only Mangrove, Babul.
„ a, b & c Mimosa and Quebracho.

These data lead to certain speculations regarding the part played by the differently ionisable phenolic components in the fixation and penetration of tannin, yield of the leather, fixed, loosely and freely held tannins and the hydrogen bonding theory of vegetable tanning.

From the data obtained for total m.eq. of phenolic -OH, the % phenolic -OH was calculated and this data compared favourably to the data obtained earlier by another technique indicating the soundness of both the techniques for determining the % phenolic hydroxyl group in polyphenolic bodies.

Acknowledgement :

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NATURE OF TANNINS IN TERMINALIA CHEBULA*

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SUMMARY

From acetone extract of myrab, three distinct fractions were isolated by liquid/liquid extraction with ethyl acetate at different pH values. The molecular wt. bound water and titration curves of all these fractions were studied before and after hydrolysis. It would appear from the values obtained for the different fractions that the tannins in myrab are fairly complex in nature, and exist in varying degrees of agglomeration. They also differ considerably in their susceptibility towards hydrolytic breakdown.

Tannins in vegetable tan materials exist mostly in complex form in varying degrees of dispersion and polymerization. These tannins are acidic in nature and in natural tanstuffs they may occur in free state or in form of salts with the organic or inorganic bases present. In order to extend our knowledge of these Indian tan materials, this work was undertaken to separate the tannins of Myrobalan nuts (Terminalia Chebula) into fractions of more simple composition. Fractionation of tannins is possible in many ways but in the present work it was decided to extend the methods of Philips[1] and Asquith[2] which involved—

(1) a preliminary treatment with acetone which would be expected to extract most of the tan materials and possibly some of the non-tan organic acids,

(2) evaporating to dryness under vacuum,

(3) dissolving in water and filtering off any insoluble material, followed by,

(4) extraction of the aqueous solution at various pH values using ethyl acetate as the extracting solvent.

The present work seeks to elucidate the nature of these fractions by determining the molecular weight, degree of hydration and titration curves and by using hydrolysis as a means of further simplyfying the components.

Experimental :

The acetone extract of myrob was prepared by shaking about 500 gms. of crushed myrob nuts with about 2000 cc. of acetone

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for 24 hours at room temperature. After standing overnight the solution was filtered through cotton wool and distilled under vacuum when a yellowish brown extract was obtained. The extract was finally dried in a vacuum desiccator and weighed 70/75 gms.

50 gms. of this extract was then dissolved in a litre of distilled water. A pale white precipitate was formed which was found to be chebulinic acid. In order to facilitate complete precipitation of chebulinic acid, the solution was stirred vigorously by an electric stirrer for 3-4 hours. The precipitate was subsequently filtered off and the filtrate brought to pH 7 by the addition of sodium hydroxide.

The extraction was carried out with ethyl acetate at this pH in a specially designed liquid liquid extractor for one week. After this time fresh lots of ethyl acetate failed to extract any appreciable amount of tannin. Hence the ethyl acetate layer was separated, vacuum distilled and dried when 4/5 gms. of light red crystalline solid was obtained. The water layer after the separation of the ethyl acetate layer was then brought down to pH 1 by the addition of sulphuric acid. The extraction at this pH was then continued as before for 3 weeks when the extraction was found to be complete, as fresh changes of ethyl acetate were not coloured at all. The ethyl acetate layer was separated as before and on distillation and drying under vacuum yielded about 15-18 gms. of a dark brown amorphous powder of very hydroscopic nature. The remaining aqueous solution which has now been successively extracted with ethyl acetate at pH values of 7 and 1 is termed the ethyl acetate insoluble portion. These ethyl acetate insoluble fractions contained much salt due to the addition of strong acid to change the pH values and hence during hydrolysis much of the ethyl acetate might be converted to acetic acid. Accordingly before hydrolysis it was thought advisable to remove the salt by extracting the tannins with methanol. The residual liquor i.e., the ethyl acetate insoluble fraction was therefore evaporated to dryness under vacuum and was then extracted with methanol. On drying this fraction yielded 8/12 gms. of dark yellow powder.

Molecular weight, bound water and titration curves of the fractions before and after hydrolysis

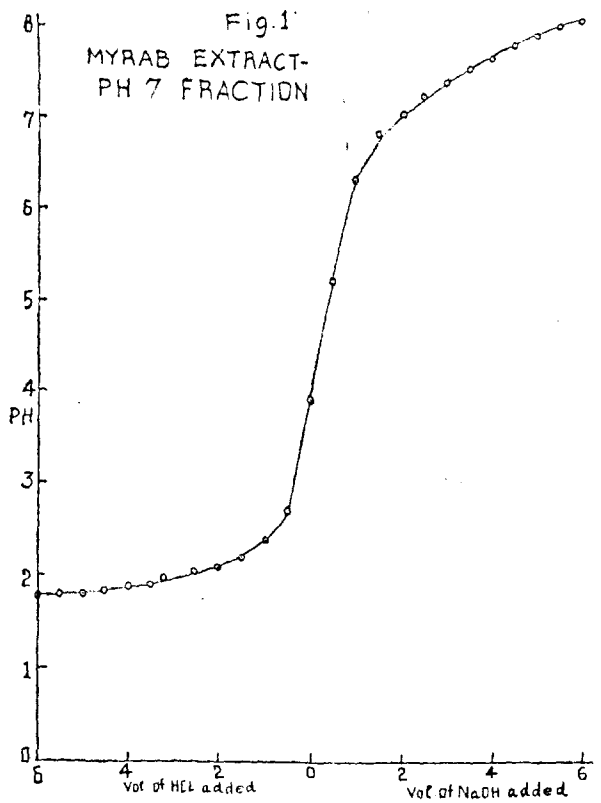
A systematic study of the titration curves, molecular weights and bound water was made with the three fractions obtained as above. In carrying out the potentiometric titrations, care was

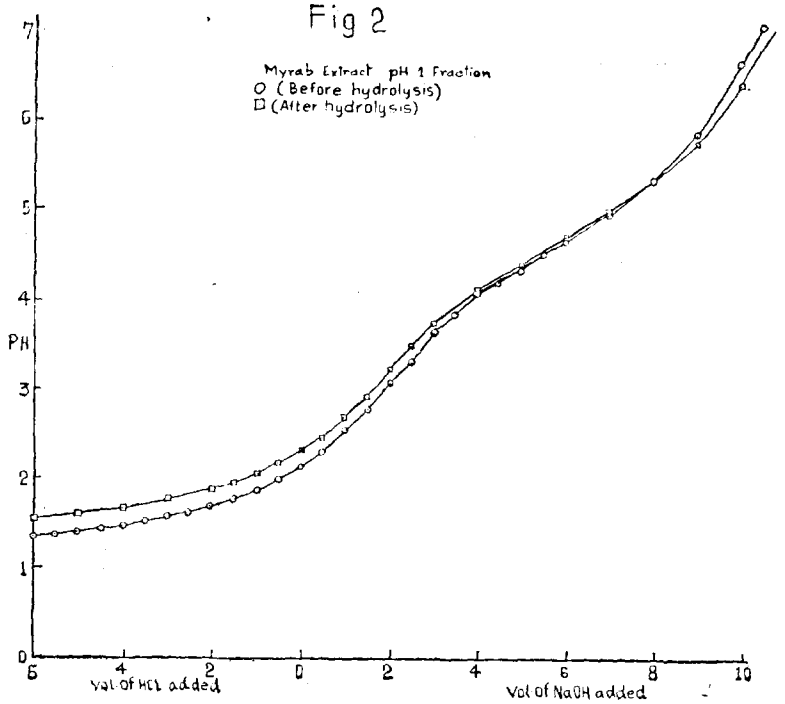
taken to maintain the total soluble content of the fractions the same in each case. A portion from each of the above three fractions was set apart and continuously boiled for one week under a reflux for initiating hydrolysis of the compounds if possible. The above studies were then repeated on these hydrolysed fractions after adjusting the total soluble concentrations to the same level as before.

The potentiometric titrations were carried out by taking 20 ml. of each of the above fractions and using N/5 reagents. Titration curves were obtained by plotting pH against ccs. of acid or alkali added. The titration curves before and after hydrolysis of all the fractions are given in Figs. 1 to 3.

Yield of different fractions obtained from 50 gms. of acetone extract.

Water insoluble	: 8-10 gms.	pH 7 fraction	: 4-3 gms.
pH 1 fraction	: 15-18 gms.	Methenol fraction	: 6-8 gms.





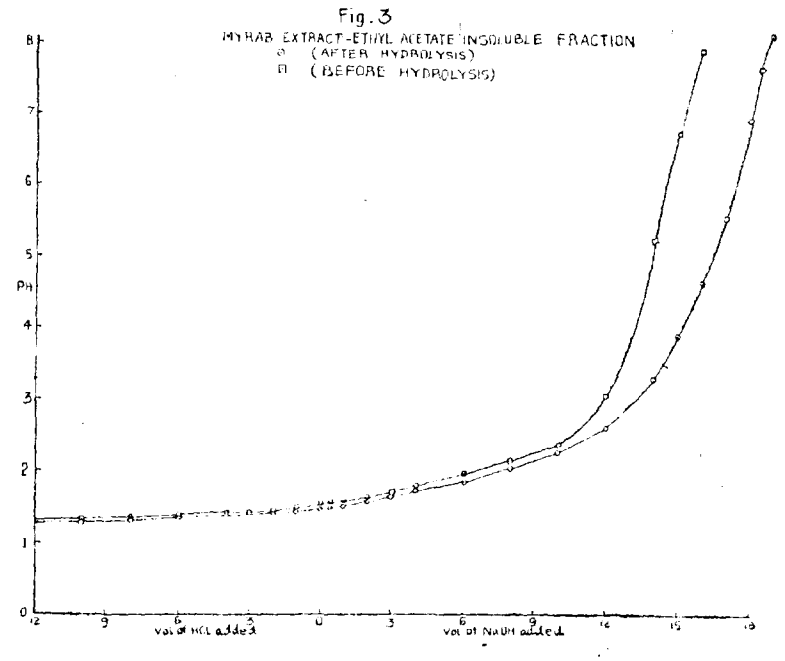


TABLE I:

Ethyl acetate extraction of myrab.	Molecular wt. Initially	Molecular wt. after hydrolysis.	Bound water per gm. of total solubles. Initially	Bound water per gm. of total solubles. After hydrolysis.
pH 7 fraction	1141	201	15.65 gm.	3.94
pH 1 „	207.8	211.9	5.99	0.85
Ethyl acetate insoluble fraction	125.4	93.97	5.62	16.15

DISCUSSION:

From the results in Table I it would appear that tans in myrab are fairly complex in nature and exist in varying degrees of polymerization. Bulk of the tannin comes out at pH 1. This fraction appears to be fairly stable to hydrolysis. It is of interest to note that the general nature of the titration curve of this fraction is very much the same as that of the ordinary myrab, which is fairly well buffered. Calculation of buffer index of the pH 1 fraction both before and after hydrolysis show that the fraction remains more or less unchanged after hydrolysis which is also obvious when the two curves are super imposed. There is a slight rise in initial pH of the pH_1 fraction after hydrolysis but no change in the acidic nature of the curve is observed which remains more or less buffered to the same extent. As this fraction constitutes the majority of myrab tannins with the characteristic titration curve of myrab, it may be termed as the active tannin constituent of myrab which is responsible for imparting the general characteristics of the material.

It is further observed that extraction at the higher pH value yields a tan fraction of higher molecular weight with a correspondingly high degree of hydration. It appears therefore that most of the aggregated tans of high molecular weight are being extracted at pH 7. That they are indeed complex aggregates is further shown by the smaller molecular weight obtained when this fraction is hydrolysed and the results show that the hydrolysis product is most likely the same as that extracted at pH 1 by ethyl-acetate. The titration curve of this fraction before hydrolysis indicates the difference in its nature. The sigmoid shaped curve obtained show a region of slow rise at the beginning and towards the end of the titration, a sharp rise being recorded at

the middle portion of the curve. By and large it is evident that this fraction appears to be least buffered. Since the corresponding titration curve after hydrolysis could not be obtained for shortage of the sample further interpretation is not possible.

In both the cases it is observed that on hydrolysis, the degree of hydration of the particle is lessened. Since water molecule is co-ordinated to the hydrophilic groups of the tan particles, it is expected that with the break down of the aggregates, less amount of water will be bound.

The ethyl acetate insoluble fraction, contrary to the expectation however contains the simplest units of myrab tannins, as indicated by their molecular weight. These further break into simpler components on hydrolysis and the molecular weight of the primary unit appears to be near about 100. It would be of interest to study the tanning characteristics of these fractions and by such studies it may be possible to compare this fraction with the semi-tan and non-tan portions of myrab liquor. Tans in this fraction being of small molecular weight are capable of quick penetration into the structure of pelt and appear to be rather prone to hydration which again facilitates diffusion. Hydrolysis does not seem to affect the chemical constitution of the fractions but seems to act as a means of effecting depolymerization. This is also evident from the nature of the titration curves of this fraction both before and after hydrolysis which do not record any significant variation.

Thus tannins in myrab exist in varying degrees of dispersion and hydration and are extractable at definite pH values. Generally speaking 3 distinct fractions can be isolated with typical molecular weight and size of the tannin together with their characteristic stability towards simple hydrolysis. Unlike the condensing type of catechol tannins, tannins in myral are of hydrolysable nature and their astringency therefore will depend upon their initial aggregation and the extent of their hydration.

Director's Lab.
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BACTERIAL PENETRATION IN RAW HIDE DURING STALING

S. C. NANDY, S. N. SEN & B. M. DAS

SUMMARY

The nature of penetration of bacteria in a cow hide during staling in stack in a high humid atmosphere were studied microscopically. The penetration was found possible both from the flesh side and hair side though initially bacteria enters from the flesh side. Those bacteria penetrated from the hair side are probably partially responsible for the hair slip and grain damage. The large numbers of chromogenic bacteria that are present in the raw hides or are contaminants from dust or water may have some effect on the decomposition of the raw hides.

The question as to whether bacteria attack hides and skins entirely through flesh side or through grain side or through both during staling is still undecided. Elucidation of this particular point would help us to understand the process of staling more clearly and to take necessary steps to make the curing process more effective. Robertson[1, 2] is of the opinion that bacterial attack and penetration takes place almost through flesh side and that the grain side is protected from bacterial attack due to the hair and the horny layer of epidermis. She also ascribes the present system of curing by the application of salt to the flesh side only to this reason. Probably it is true at the initial stages of staling the bacteria get a more suitable substrate in the flesh to attack but with the elapse of time, it is possible that bacteria penetrate also from the grain side through the epidermal layer. This assumption appears to be plausible on account of the fact that appreciable hair slip does not occur before 24 hours of staling. The object of the present work was to find out the nature of bacterial attack during the staling of raw hides and the mode of penetration of bacteria into the hide structure. Studies in these directions have been made microscopically on sections cut from samples staled for different periods.

EXPERIMENTAL :

Freshly slaughtered cow hide was taken from the slaughter house, fleshed and then washed well in order to free it from blood, dung etc. which promote bacterial growth by serving as a nutritive food material for bacterial spores and hence it was expected that

bacterial action on the washed and fleshed hide, would be much less than that on the unwashed one. The hide pieces were washed and fleshed in order to have a uniform nature of bacterial distribution and penetration. The hide was cut into pieces and then blotted in the folds of a blotting paper and kept in a closed moist chamber at 30°C for staling. The pieces were kept in stack with flesh side up and some pieces were weighed for the counting of bacteria. Hide pieces staled for 3, 24, 48 and 72 hours were taken in sterile churning bottles with ten times their weight of a sterile distilled water and shaken for 2 hours. The extracted liquors were then diluted to different extents and the bacterial counts were made in duplicates. The medium used was that of ordinary Agar medium at pH 7.2 The counts were made after 48 hours of incubation at 37°C. The bacterial counts are expressed as numbers of bacteria per ml. of extracted liquor. The results are given in Table I.

To find out the mode of penetration of bacteria into the hide structure the pieces were preserved in formol saline at the end of different periods of staling. The pieces were then thinly sectioned at about 40-50 μ by a freezing microtome and then stained with an aqueous solution of Azure, dehydrated and finally mounted on canada balsam. These were then studied under the microscope and the results are represented by photomicrographs.

TABLE I

Hours of staling	Total no. of bacteria per ml. of extracted liq.	Chromogenic bacteria per ml. of extracted liq.	Percentage of chromogenic to total no. of bacteria.
3	5,60,000	4,10,000	71.43
24	11,40,00,000	7,95,00,000	69.74
47	7,80,00,00,000	5,50,00,00,000	70.51
72	12,50,00,00,000	8,50,00,00,000	69.23

MICROSCOPICAL OBSERVATIONS :

Staled for 3 hours : No bacteria was found to have penetrated into the corium either from the flesh side or from the grain side after 3 hours of staling, i.e. actually after receiving from the slaughter house. The epidermis and the other structures were quite normal (Plate-1).

PLATE 1. Stain - Azure. Section - 40μ
Magnification $\times$78. Staled for 3 hours. No Penetration of bacteria into the corium. Epidermis normal.

Staled for 16 hours : After 16 hours of staling very limited number of bacteria were found to have penetrated into the fibre structure from the flesh side. No penetration of bacteria was observed from the grain side. The types of bacteria were found to be of long chain forming bacilli and penetrated to a little extent into the corium. The condition of the epidermis was practically unchanged (Plate-2).

Staled for 24 hours : In this case it was observed that the penetration of bacteria into the corium from the flesh side increased to a considerable extent. Other than the long bacilli some cocci were also found to have penetrated. But on the other hand, a large number of bacteria have penetrated from the hair side also into the corium. A large number of bacteria were detected into the epidermis with their continued progression towards the corium. The types of bacteria were long chain forming rods, short rods and some cocci. These bacteria were found to have penetrated into the junction of the corium and epidermis, just below the entire epidermal surface with more or less uniform distribution. It was observed that, in the middle portion of the corium, the bacterial population was much less in comparison with that of the epidermis

side and the flesh side. Only the long chain forming rods were found to have penetrated into the middle portion of the corium. (Plate-3).

PLATE 2. Stain - Azure. Section - 40μ
Magnification $\times$840. Staled for 16 hours. Penetration of long chain forming rods are found from the flesh side.

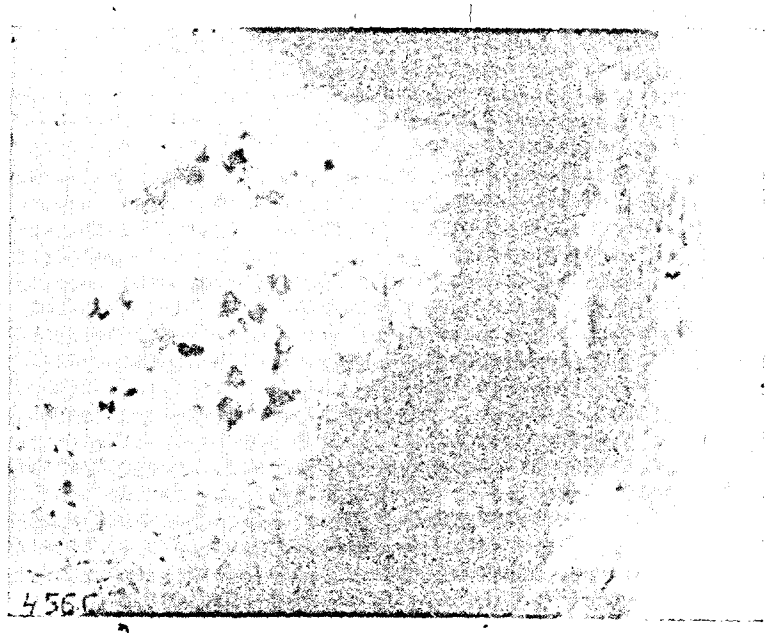

PLATE 3. Stain - Azure. Section - 40μ
Magnification $\times$840. Staled for 24 hours. Heavy penetration of long and short rods are found from the hair side just below the epidermis. Epidermis not so affected.

Staled for 48 *hours* : The same picture of bacterial penetration was found as that of 24 hours staling but with much more bacterial population. The penetration of bacteria into the middle portion of the corium were found to have increased. The epidermal layer was separated from the corium in most of the places producing an empty space between them. (Plate-4).

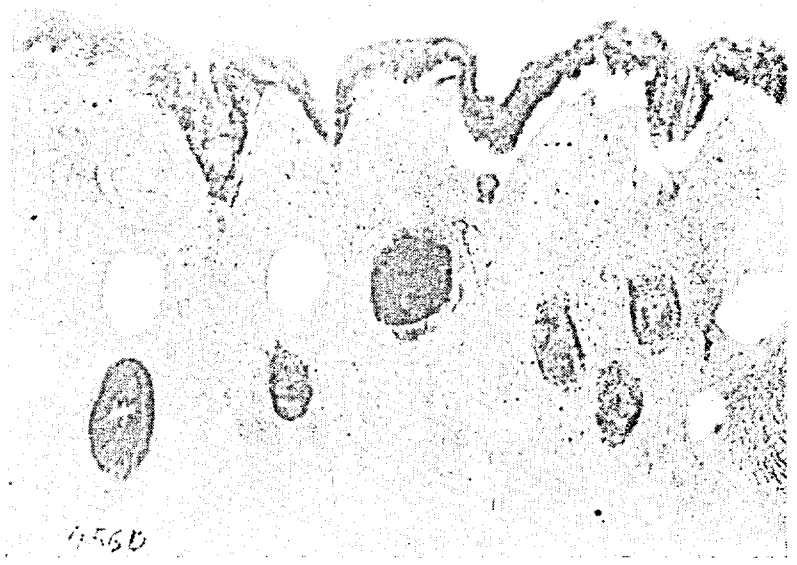

PLATE 4. Stain – Azure. Section - 45μ
Magnification $\times$78. Staled for 48 hours. The epidermis is found to have been detached from the corium in a number of places.

Staled for 72 *hours* : The penetration of bacteria into the corium was thorough throughout the entire structure. Most of the bacilli were found to have formed spores. Terminal spores were also found in some of them indicating the presence of anaerobic types of bacteria. The epidermis in this case was entirely removed from that of the corium and the thickness of the hide was reduced to a considerable extent. (Plate-5).

It was observed that there was no ' hair-slip ' upto 24 hours of staling after which the ' hair-slip ' began to develop, and hairs slipped easily in cases of 48 and 72 hours of staling. While soaking, the hide pieces staled for 48 and 72 hours were found to be separated into two layers, the upper layer being the hairs with the entire epidermis.

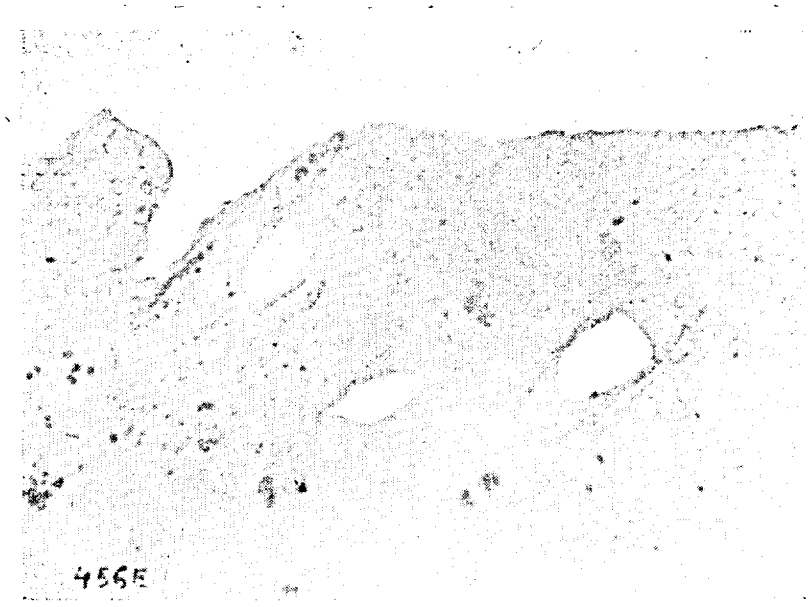

PLATE 5. Stain – Azure. Section - 50μ
Magnification $\times$78. Staled for – 72 hours. The epidermis is entirely removed from the Corium.

Discussion :

From Table I it can be found that the numbers of bacteria counted from the soak liquor increased rapidly with the staling period. The chromogenic count also increased more or less in the same direction. It was interesting to note that the percentage of chromogenic bacteria to that of total number were fairly constant throughout the entire period of staling. Most of these chromogenic bacteria observed were of micrococcus or sarcina group. Moreover bacteria of coccus type were also found to have penetrated into the hide substance. Probably these chromogenic bacteria do play some role in the decomposition of the raw hide.

By summarising the microscopical observations it can be found that the bacterial attack inside the hide structure also increased rapidly with different periods of staling although the rate was much less at the initial stage. The hide piece was quite normal after three hours of slaughter without having any bacterial penetration. After 16 hours of staling, a few bacteria were found to have penetrated from flesh side. But after 24 hours quite a different picture was observed. A large number of bacteria had penetrated from the hair side and accumulated just

below the epidermal layer. The penetration of bacteria from the flesh side was increased from that of previous case but the bacteria at the flesh side were more thinly populated than those at the hair side. Even then the epidermis was practically undetached from the corium. After 48 hours, however, the epidermis was peeled off in a number of places and accumulation of bacteria was found on the surface of the corium just below the epidermis. The penetration of bacteria in the middle layer was comparatively increased. After 72 hours, the epidermis was completely removed from the corium and most of the bacteria were found to have formed spores.

Robertson carried out experiments to show the mode of penetration of bacteria into raw hide under different variable conditions. She has concluded that, except with certain special types of bacteria, their penetration takes place almost entirely from the flesh side and she has put forth this fact as the reason for the practice of salting hides on the flesh side. Our work reveals that bacteria first penetrate from the flesh side but after 24 hours different types of bacteria penetrate also from the grain side through the epidermis into the corium. If these bacteria on the grain side would have penetrated from the flesh side, the population of bacteria adjacent to the flesh side would be much more than that of the grain side and the penetration into the middle layer of corium would also be considerable so as to have a regular stream of bacteria. At the end of 48 hours, the action of these bacteria at the epidermis side was quite pronounced as was evident from the detachment of the epidermis from the corium which action might probably have started and taken place increasingly after 24 hours.

No doubt, the penetration of bacteria is much easier from the flesh side than from the hair side but our work shows that, it cannot be said that bacteria do not penetrate in any condition from the hair side during the staling period. The reasons that Robertson had given for the inhibition of bacterial penetration from the grain side, however, may be initially effective for some time after which bacteria penetrate from the hair side also. The horny nature of the epithelial cells may give a protection to the bacterial attack on the grain layer initially but keeping up hides for staling in favourable moisture and temperature after well washing is conducive for the horny layer on surface to become susceptible to bacterial action and subsequent penetration. Of course if the moisture content or the humidity is not sufficient the epidermal layer would remain stiff and may not give access

of bacterial penetration. Moreover these bacteria which enter from the hair side are probably responsible for the hair slip and other damages caused on the grain surface.

The usual practice of salting raw hides and skins on the flesh side is most probably not due entirely to the reason adduced by Robertson. The principle of curing hides and skins by salting is to check bacterial growth by quicker absorption of salt and dehydration of the hides and skins. McLaughlin and Theis[3] had pointed "we are vitally interested in the salt absorption rates during the first few hours of treatment, because the greater the salt absorption during the first few hours the quicker the curing action". They have also shown that the amount of salt absorbed in 24 hours when hair side alone was salted was only one twenty-fifth of what was absorbed when the hide was salted on the flesh side alone or on both sides. It was also noted by them that the salt absorption when hide was salted on both sides was no greater than when salted on the flesh side only. Strandine, de Beukelaer and Koonz,[4] Kritizinger and Vanzyl[5] have also shown that the penetration of salt from the hair side was practically negligible. McLaughlin and Theis further showed that movement of salt and water was in opposite direction, the salt moving into the hide, the water out. Dehydration is effected only when the salt moves into the hide. So naturally the dehydration would be delayed with slow absorption of salt which factors are against the principle of curing. These points clearly indicate the reason of salting hides and skins from the flesh side is to produce quick and effective curing.

Bacteriological lab.
7—5—1956.

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2. Idem Leather World, **26**, 255 (1934).
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A STUDY OF THE EFFECT OF SHELL LIME ON THE FIBRE STRUCTURE OF THE PELT IN LIMING COW HIDES

S. K. SARKAR, S. K. MITRA & B. M. DAS

SUMMARY

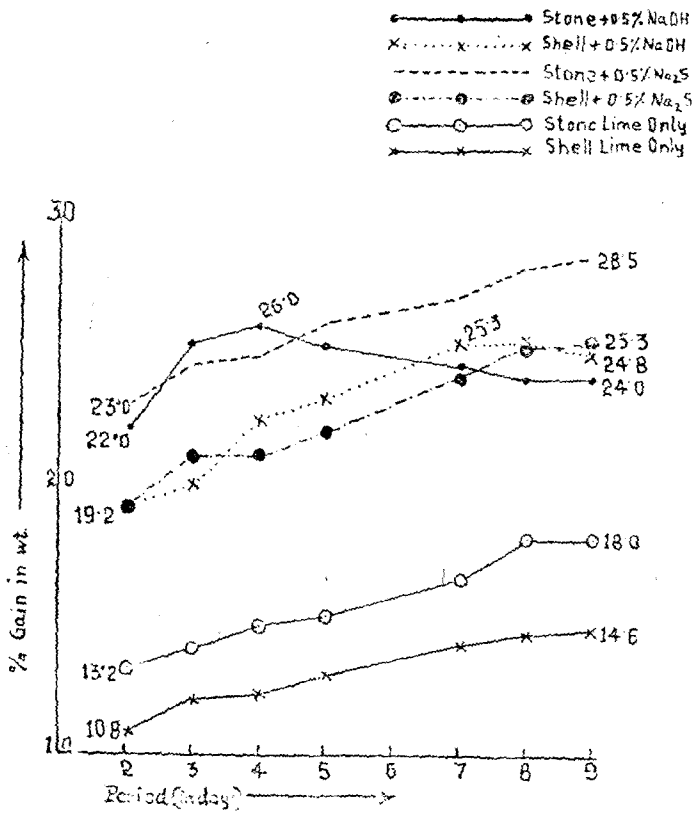
The effect of shell lime on the fibre structure of the pelt and the resultant leather in liming cowhides for E.I. tanning has been studied and compared to stone lime. The study has revealed that shell lime is mellower in action than stone lime. Shell lime produces comparatively less smooth grain surface but reorients the fibre structure of the pelt in a way which appears to be suitable for the manufacture of E.I. tanned kips. No special advantage is gained by sharpening shell lime liquor with 0·5% Na_2S, while the addition of even this quantity of NaOH to the lime liquor is detrimental to the grain fibres and the hyaline layer of the pelt. Stone lime on the other hand produces finer and smoother grain surface and a more compact grain layer than shell lime.

In South India, shell lime is usually used for liming hides and skins. Shell lime is obtained by burning sea-shells and its CaO content is somewhat lower than that of stone lime used in other parts of the country. While information regarding the special advantage of its use over stone lime is not available, it is the common belief of the E.I. kip tanners that shell lime is very suitable for liming E.I. kips and skins. The present work was undertaken to obtain details on the above points, taking into consideration its effect on the fibre structure of the pelt destined for E.I. tanned kip.

Experimental materials were taken from the butt portion of a wet salted cow hide. Three sets of experiments were carried out with six small cut pieces from corresponding positions, measuring 4" × 6" each, using 15 per cent shell lime (available lime 26%) and stone lime (available lime 50%) on the soaked hide weight separately with and without the addition of sharpening agents. In the first set, lime liquors were not sharpened whereas the liquors under sets 2 and 3 were sharpened with 0.5% Na_2S and 0.5% NaOH respectively. All the pieces were limed for nine days at the laboratory temperature varying between 28°C and 30°C. At the end of the experimental period the limed pieces were unhaired, washed in 2-3 changes of water, delimed completely with 1% boric acid and then tanned in the same way and finished as E.I. tanned leather. Samples for histological study from all the pieces were collected after liming as well as after

tanning and finishing. The histological technique as adopted by the Central Leather Research Institute was followed during the study.

The percentage gain in weight of the limed pieces over raw weight was noted throughout the experimental period. The increase of weight during liming has been plotted on the curve given below.



It will be observed from the graphical representation of the results that in all the three sets, the gain in weight using shell lime was lower than that obtained with stone lime, viz. 14.6%, 25.3% and 25.3% against 18.0%, 28.5% and 26.0% respectively. In the case of unsharpened lime liquors and the liquors sharpened with 0.5% Na_2S, the weight gained progressively throughout the experimental period, stone lime showing higher figure all along; and where the lime liquors were sharpened with 0.5% NaOH the peak was reached on the fourth day with stone lime and only on the seventh day with shell lime, after which the loss in weight started due obviously to the solution of hide substance. It, therefore, appears that shell lime either used alone or in conjunction

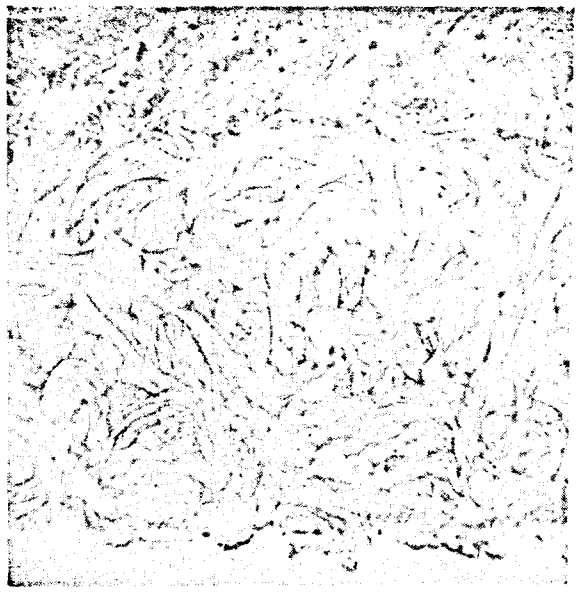


FIG. 1
Cow hide limed with 15% Shell lime only

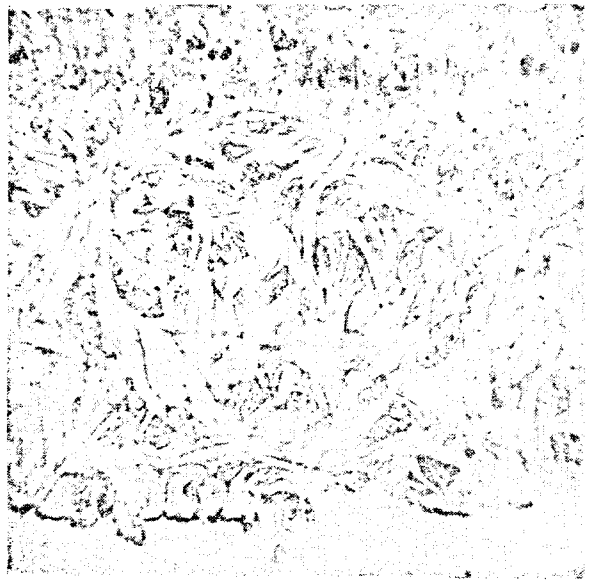


FIG. 2
Cow hide limed with 15% Stone lime only

FIG. 3
Cow hide limed with 15% Shell lime and
0·5% Sodium Sulphide

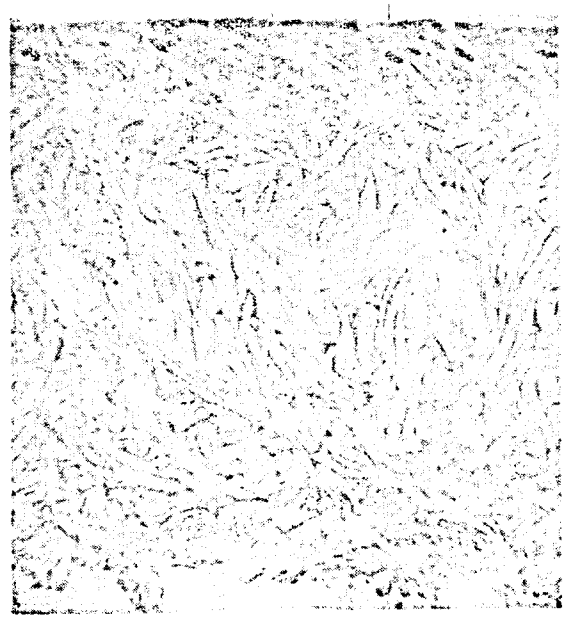


FIG. 4
Cow hide limed with 15% Stone lime and
0·5% Sodium Sulphide

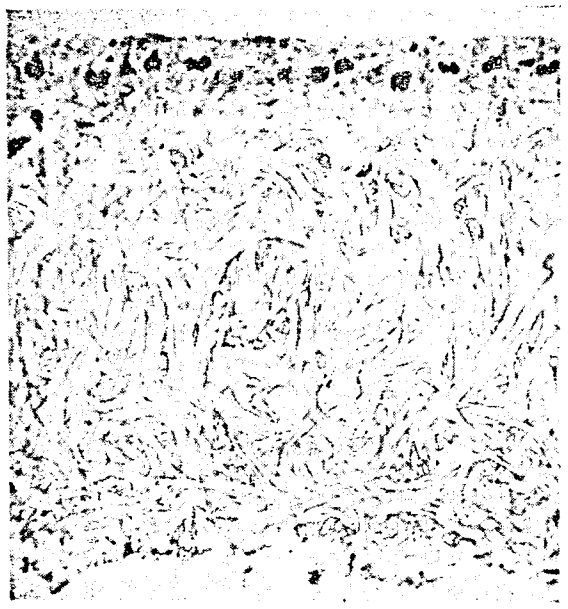


FIG. 5
Cow hide limed with 15% Shell lime and
0·5% Caustic Soda

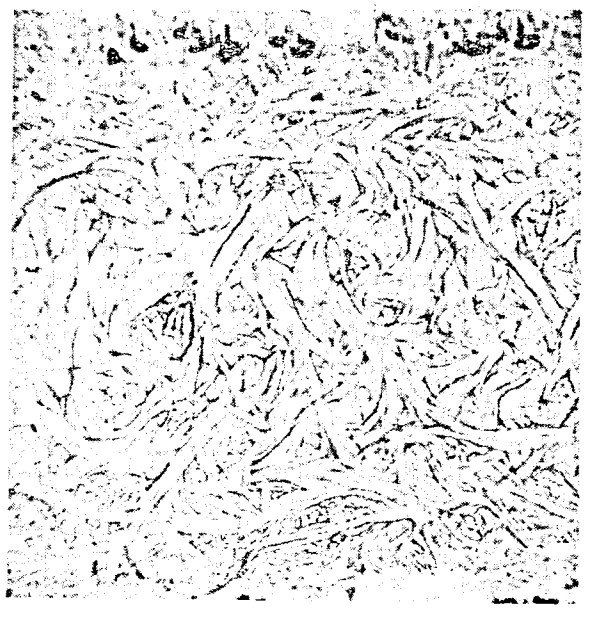


FIG. 6
Cow hide limed with 15% Stone lime and
0·5% Caustic Soda

with sharpeners is mellower in action and produces less plumping of the pelt than the stone lime.

From the microscopical appearance of the limed as well as tanned pieces tabulated in Tables I and II and illustrated by photo-micrographs, it will be seen that stone lime produced smoother and finer grain surface, and thicker grain layer than the shell lime. Excepting the case where NaOH was added to the lime liquor, stone lime reoriented the fibre structure to a higher angle and opened the collagen bundles of corium and also the fine fibres of the grain to a greater extent than the shell lime; the fullness of the fibres and compactness of the weave were greater in the case of the former. Where NaOH was added, the stone lime damaged the grain surface more than the shell lime, but the fibres connecting grain and corium were damaged to the same extent in both the cases. Caustic Soda, however, opened the collagen bundles to a lesser degree than sodium sulphide. After tanning, the conditions of the fibre structure were more or less the same, but the percent decrease in grain thickness of the leather after drying and finishing was found to be more where stone lime was used, viz. 28.0 to 33.3% making the grain layer too compact and less pliable. With shell lime this decrease did not exceed 14.2% and the grain layer appeared to be less compact but more pliable than the former. This partly accounts for less smoothness of the grain surface obtained by liming with shell lime. No appreciable difference with regard to resticking of the tanned fibres was however noticed.

It has been specified[1] that so far as micro-structure is concerned, a good quality E.I. tanned kip should be characterised by low angle of weave lying between 30°-40°, a fairly compact weave (neither very compact nor loose), a less compact grain layer, uniform merging of the grain fibres into corium, complete splitting at the grain and only fair amount towards the flesh without appreciable amount of resticking of fibres. It will be evident from the present investigation that although shell lime produces comparatively less smooth grain surface, a fibre structure more or less similar to that stated above can only be obtained by using shell lime liquor. It also appears that no special advantage is gained by sharpening the shell lime liquor with either sodium sulphide or caustic soda. This investigation further corroborates the popular belief that shell lime is better suited for the manufacture of E.I. tanned kips.

Microscopical lab.

12—3—1956.

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TABLE I.

Microscopical Appearance of the Limed Pieces.

	Composition of lime liquor	Angle of weave	Splitting up of fibre bundles	Fullness of fibre bundles	Compactness of weave	Merging of grain into corium	Thickness of grain layer	Fibres connecting grain and corium	Condition of the grain surface
I	Stone lime alone	About 45°	More than medium amount	Fairly full	Fairly compact	Fairly uniform	0·584 mm	More split up than II ; no damage	Smoother than II
II	Shell lime alone	Below 45°	Less than I	Less than I	Less than I	do	0·541 mm	Less split up than I ; no damage	Less smooth rather coarser than I
III	Stone lime plus 0·5% Na_2S	Above 45°	Large amount	A little less than full	Compact	Uniform	0·546 mm	More split up than IV ; no damage	Smoother and finer than IV
IV	Shell lime plus 0·5% Na_2S	A little less than 45°	Less than III	Less than III	Less than III	Fairly uniform	0·524 mm	Less split up than III ; no damage	Less smooth than III
V	Stone lime* plus 0·5% NaOH	45°	Medium amount	Full	Compact	Not uniform	0·516 mm	Less split up than VI ; slightly damaged	Partly damaged
VI	Shell lime* plus 0·5% NaOH	45°	do	A little less than V	Fairly compact	Better than V	0·438 mm	More split up than V ; slightly damaged	Slightly damaged

* No. V appeared more translucent than VI.

TABLE II.

Microscopical Appearance of the Leather pieces.

Nature of lime liquor used	Angle of weave	Splitting up of fibre bundles	Fullness of fibre bundles	Compactness of weave	Merging of grain into corium	Thickness & compactness of grain layer	Fibres connecting grain and corium	Condition of the grain surface	Resticking of fibres	% decrease in grain thickness after taning and finishing
(I) Stone lime alone	About 45°	More than medium amount	Fairly full	Fairly compact	Fair	0·391 mm ; compact	Highly split up ; no damage	Fine & smooth	Slight amount	33·0
(II) Shell lime alone	Below 45°	Medium amount	Slightly less than I	Slightly loose	do	0·464 mm ; less compact than I	Large splitting ; no damage	Less smooth and less fine than I	Small amount	14·3
(III) Stone lime plus 0·5% Na_2S	About 45°	Large amount	A little less than full	A little more than fairly compact	Fairly uniform	0·391 mm ; compact	Highly split up ; no damage	Fine & smooth	Nil	28·3
(IV) Shell lime plus 0·5% Na_2S	Less than 45°	More than medium amount	do	Fairly compact	do	0 464 mm ; less compact than III	Same as III	Less smooth & less fine than III	Slight amount	11·4
(V) Stone lime plus 0·5% NaOH	Less than 45°	Medium amount	Fairly full	Fairly compact	Poor	0·344 mm ; loose	Small splitting ; dainaged	Totally damaged	Slight amount	33·3
(VI) Shell lime plus 0·5% NaOH	Less than 45°	Slightly less than V	do	Slightly loose	do	0 387 mm ; loose	do	Partly damaged	Small amount	11·7

CLASSIFIED ABSTRACTS

RAW MATERIALS

ON SOME ASPECTS OF HIDE PRESERVATION*—*S. C. Nandy, S. N. Sen and B. M. Das. J.L.T.A. (India)*, **4**, 2, 45, (1956) : If leather of highest quality is to be produced, the raw hides and skins must be kept free from putrefaction both before and during the process of leather manufacture. The correct amount of salt to be used for curing, the effect of moisture content, humidity, temperature and other factors on their subsequent preservations which are points of great importance have been studied. Investigations have also been made for suitable substitute for Khari salt and for prevention of mould growth during preservation after pickling.

DEAD AND SLAUGHTERED HIDES—HOW TO DISTINGUISH THEM*—*J. K. De and Fatehar Rahman, J. L.T.A. (India)*, **4**, 2, 43, (1956) : In India raw hides are obtained from dead and slaughtered cows and buffaloes. After the partition of India, the availability of slaughtered hides fell down as a result of which the Chrome Tanning industry has to face a serious set back for getting quality raw hides for the production of quality leathers. This shortage led the hide collectors to adopt unfair means of passing the raw hides in the disguise of slaughtered ones. It is very difficult for a tanner to differentiate between the dead and slaughtered hides. A very simple test, however, is to cut down a piece of both dead and slaughtered hide and to examine the cross section. Slaughtered hides will be found to be white and opaque but dead hides will appear to have a bit reddish hue with minute spots of blood. Another significant identification is by the butcher's slaughtering cut at the throat which can be marked in case of slaughtered hides. But many flayers of dead cattle purposely make such a cut at the throat. In the tanning processes, it is possible to distinguish the slaughtered and dead hides by the colour of the pelt before and after fleshing provided the slaughtered hides are wet salted and stored not more than a week. Other signifying marks of dead cattle hides are vulture marks, full length of legs with hoofs and ears attached to the head pieces. With help of the presence of these on the hides, a tanner can also distinguish the dead hide from slaughtered one.

* Abstracts of papers presented at the symposium on Chrome Tanning Industry and Tanning processes held at Calcutta on 22nd to 24th April 1956 under the auspices of the Leather Technologists' Association (India).

TANNING

STUDIES IN CHROME TANNING*—*V. P. Pandit, J.L.T.A. (India)*, **4**, 2, 72, (1956) : Many factors contribute toward the making of good quality chrome upper leather. One of them is chrome tanning itself and subsequent result on the chrome content of finished leather. From the chrome tanning under different conditions, it has been attempted to recommend certain methods of chrome tanning. The hides after liming and bating were pickled and tanned with chrome liquor in 3 instalments under different conditions such as 26% basic liquor, 21% basic liquor by draining pickle, 26% basic liquor reduced acid in pickle, 36% basicity and increased chrome and 46% basicity and increased chrome. The tanned leathers were finished and analysed. It is concluded that in addition to other factors, the chrome content of any chrome tanned upper leather has a great bearing on the final quality of the leather. The above chrome content is greater affected by the following factors : (1) the acidity of the pickling process. (2) The acidity of the chrome tanning drum. (3) The basicity of the chrome tanning solution at the end of tanning and (4) The amount of chrome that is added. The pickle acid and the acidity of chrome tanning solution should be so adjusted that the basicity of the residual solution at the end of chrome tanning should be 35-40%.

The chrome addition should be on the basis of 2.1-2.5 lbs. Cr_2O_3 per 100 lbs. limed pelt. By calculating the dilution of the original liquor and by analysing the residual liquor, it is desirable to bring about an 80% exhaustion of the total chrome added. The finished leather in order to have a full feel should have Cr_2O_3 content ranging between 4.0-5% on air dry weight basis. It is most necessary to allow liquors to account at least for a week. The particular period required for any tannery can easily be determined. If more basic liquors are used, they tend to deposit more chrome in the leather should be determined by the effect on the grain. Excessive increase in basicity tends to produce a coarse grain.

NEUTRALISATION OF CHROME LEATHER*—*J. Ghosh. J.L.T.A. (India)*, **4**, 2, 69, (1956) : The principal object of neutralisation is to reduce the cationic charge after chrome tanning upto a degree suitable for desired penetration of anionic dyestuffs and fat emulsion. For this, choice of neutralisation agent is an important factor in the process of neutralising of chrome leather. Salts of higher dissociation constants are not recommended, for neutralisation since there are considerable reversible reactions and the leather surfaces are again charged with positive charges due to diffusion of cationic radicals from the inner portions in course of further hydrolysis during subsequent washing. Chrome tanning with masking agents help to check the difficulty.

TWO BATH CHROME TANNING PROCESS FOR THE MANUFACTURE OF GLAZED KID LEATHER AND THE MODERN DEVELOPMENT OF ITS TECHNIQUES AND METHODS*—*J. C. Deb and B. M.*

Das. J.L.T.A. (India), 4, 2, 64, (1956) : The process of manufacturing glazed kid by two baths, the chrome bath and the reduction bath as patented by Schultz, is described in details. In America, some variations have been made in the process from the original Schultz's recipes. Some tanners carry on the two bath process in a single drain after completion of chroming followed immediately by adding Hypo in the same chroming bath and adding HCl in 4 instalments at an interval of 15 mins. Dr. Belavsny's process is another best known process of combined two bath and one bath tannage. Some tanners use the syntan after the Hypo treatment. The adjustment of pH according to the desired properties of leather is important. Experiments on pilot plant scale at the Central Leather Research Institute have been carried out following 3 foreign and 4 original processes according to Indian climatic condition and raw materials and found to produce good leather. The important factors which can effect the quality of the leather are pointed out.

SOME ASPECTS OF THE ULTRA-VIOLET ABSORPTION SPECTRUM OF CHROME* LIQUORS—*D. Ramaswamy. J.L.T.A. (India)*, 4, 2, 52, (1956) : The ultra-violet and differential ultra-violet absorption of basic chrome solutions have been investigated and their possible applications in studies on olation, ageing and the nature of olatted complexes are outlined.

TANNING OF GELATIN BY CHROME ALUM. II. FIXATION OF CHROMIUM ON GELATIN—*A. M. Venet and J. Pouradier. Bull. Soc. chim. Fr.* 1955, *No.* 10, 1336-1341. *Via. J. Appl. Chem.* 6, 2, 283, (1956) : Purified gelatin is dispersed in distilled water, adjusted to a known pH and tanned for 24 hr. at 40° with known amounts of chrome alum. The gelatin is pptd. with alcohol, set aside over-night, centrifuged and washed with 50% ethanol water. Cr and sulphate are determined, after destruction of org. matter, by conventional methods. For a given pH, the plots of unfixed Cr against fixed Cr are constant, and, if plotted as reciprocals, are linear, so that extrapolation to zero gives the max. amount of Cr which can be fixed ; below pH 3.25 this is equal to the no. of free carboxyl-groups of the gelatin. At pH between 2.5 and 5.0, 1 mol. of sulphate is fixed per 2 atoms of Cr ; below pH 2.5 more sulphate is fixed. It is concluded that between pH 2.5 and 3.25 the structure of the tanned gelatin bridge is CO_2 Cr. SO_4 Cr. CO_2. Below pH 2.5, although more sulphate is fixed, the same bridge may be present. Above pH 3.25 the number of Cr-atoms fixed exceeds the no. of free carboxyl-groups, and it is suggested that neutral and even anionic complexes may be formed.

BICHROMATE AND CHROME COMPOUNDS FOR THE LEATHER INDUSTRY*—*J.V.S. Milne. J.L.T.A. (India)*, 4, 2, 57, (1956) : Sodium bichromate is to-day manufactured in India from her indigenous sources. The bichromate should be free from the impurities such as Vanadium, Calcium sulphate, Iron sulphate, Sodium silicate, Sodium sulphate which mainly effect the tanning of leather.

Chrome liquors produced by reducing bichromate very often give inconsistent basicity, Procter value which cause variation in chrome tanning. This can be avoided by using basic chrome tan crystals which are now prepared from sodium bichromate in India having a Procter value of 96, and would be useful in the tanning of glace kid where consistent results are important. Basic chrome tan crystals prepared from chromium hydroxide give usually inconsistent results unless carefully controlled and sometimes are injurious to the tanning process. A process has been patented for producing chrome liquor from Ferrochrome.

VEGETABLE TANNING

SURFACE FILM STUDIES OF THE MECHANISM OF VEGETABLE TANNING—*A. F. Lanham and K. G. A. Pankhurst. Transactions of the Faraday Society* 52, *Pt.* 4,521, (1956) : Surface pressure, potential and viscosity measurements have been made on collagen and N-methoxy methyl nylon monolayers spread on dilute solutions of a typical flavanol tannin (from mimosa) and a digalloyl glucose tannin (tannic acid), over the pH range 2-11. Tanning is recognized by a large increase in surface viscosity and a condensation of the film which may be accompanied by a lowering of the surface potential. Experiments using a water-soluble resorcinol-formaldehyde resin as tanning material give results similar to those with natural tannings. The fact that the surface potential is not invariably changed by the tanning reaction and that tanning can take place between non-ionic reactants leads to the conclusion that hydrogen bonds, probably between the hydroxyl groups of the phenolic tannin and the carbonyls of the keto-imide backbones of the protein, are predominantly involved, and that ionic reactions, if they occur, play a subsidiary role.

SIMPLIFIED METHOD FOR THE DETERMINATION OF THE TANNING AND COMBINING FIGURE OF VEGETABLE TANNINS—*G. Reich. Leder*, 1955, 6, 228-232. *Via. J. Appl. Chem.* 6, 4, 580, (1956) : Instead of hide powder, pieces of acetone-dehydrated calf skin are used ; the values obtained correspond better with the results of practical tanning than those obtained by the standard hide-powder method. The combining figure is derived from the determination of water-sol. matter.

BARK AS A CHEMICAL RAW MATERIAL—*A. H. Vroom, Chem. Can.*, 1955, 7, *No.* 11, 74-78. *Via. J. Appl. Chem.* 6, 4, 537, (1956) : The utilisation of spruce and balsam bark available from the paper pulp industry is discussed, with reference to its fuel value and its physical and chemical components. Attention is drawn to pulpwood bark as a possible source of higher alcohols, fatty acids, waxes, tannins, phenol deriv., insecticides and fungicides, alkaloids, dispersing agents, antioxidants and other products of commercial value. (23 references).

OTHER TANNAGES

RETANNED UPPER LEATHER*—*Dr. F. Faber. J.L.T.A. (India), 4,* 2, 77, (1956) : The retanning of chrome leathers is a measure of decisive importance for improving the quality. It is our task to guide the retanning process in such a way that the customary character of European leather is preserved even in the case of retanned leather. This means :

1. Retention of the principles hitherto employed :

   (*a*) careful treatment of the hide substance in the beam house,

   (*b*) fully chromed leather as a basic principle, in order to be able subsequently to sort into pure chrome and retanned leather,

   (*c*) as large a proportion as possible of the leather should be finished without buffing with a full grain. In this connection good aniline dyeing and low covering with the finish.

2. Retanning to be brief so that adequate buffing and sufficient fullness can be obtained without altering the character of the leather too much.

3. Best possible preparation of the finish, also with buffalo leather, by dyeing in the drum or by hand in a shade as close as possible to that of the finished leather. This makes it possible to economise the pigment finish and produces a leather with a fine character.

FORMATION OF TANNINS BY THE ENZYMIC OXIDATION OF CERTAIN PHENOLIC COMPOUNDS—*W. E. Elstow D. E. Hathway and K. G. A. Pankhurst. Research,* 1955, 8, 64-65. *Via. J. Appl. Chem.* **6,** 3, 419, (1956) : The technique of studying tanning reactions by observing variations of surface of a collagen monolayer spread on to a dil. solution of tanning at a constant surface pressure was applied to the formation of tannins from simple phenolic monomers, e.g., catechol, quinol or phloroglucinol, by the action of peroxidase in the presence of H_2O_2. The over-all results were found to be compatible with the peroxidase-catalysed oxidation of phenols to quinones.

PROCESSES AFTER TANNING

ACRYLIC RESIN AND ITS TECHNIQUE OF PREPARATION*—*I. B. Sarkar, J. K. De and M. Banerjee. J.L.T.A. (India),* 4, 2, 61, 1956) : Methylmethacrylate obtained by the pyrolysis of perspex was polymerised in presence of different solvents. Their properties were studied. Next Ethyl and Butyl methacrylate were synthesised from Methylmethacrylate. Resin emulsion was then prepared out of the synthesised esters. The technique of preparing the resin emulsion was known. Some of the emulsions gave satisfactory results. Further investigation on the problems was suggested for standard products.

PRODUCTION OF OXIDATION DYESTUFFS ON FIBRES—*Cie Francaise des Matieres Colorantes (Inventors : R. L. Lantz and P. M. J. Oberlianne) (B.P.* 730, 106, 27-11-52. *Fr.* 28-11-51). *Via. J. Appl. Chem.* 6, 1, 92, (1956) : Natural and artificial textile materials are dyed in brown shades by the oxidation on the fibre of a Na salt (I) of a sulphamic acid of formula $XX^1X^2X^3$ (NRR^1). $C_6.NR^1.SO_3H$ where X are H or a halogen, alkyl, alkoxy or nitro group, R is H or SO_3H, and R^1 is H or an alkyl, Cycloalkyl or aralkyl group. The oxidation may be effected by means of an oxidising agent (*e.g.*, a chlorate), in presence also of an oxidation catalyst, *e.g.*, NH_4 vanadate, and the development of the dyestuff may be effected by treatment with an acid. Typical examples of I are Na salts of 1:4-, 1:3-, or 1:2- diaminobenzene-N-sulphonate, 2 ; 4-diaminotoluene-N^2- sulphonate, 1:4-diaminobenzene-N^1N^4-disulphonate, and a long series of new derivaties, of which the preparation is described, including 4-*chloro*-1 : 2-*diaminobenzene*-N^1-, 2 : 4-*diamino*-1-*methoxybenzene*-N^2-, N^2-*ethyl*-2 : 5-*diamino*-1-*toluene*-N^2-, N^1-*methyl*-1 : 4-*diaminobenzene*-N^4- and 2:5:6-*trichloro*-1 : 4-*diaminobenzene*-N^4--*Sulphonate.*

THEORIES

CHEMISTRY OF THE DEGRADATION OF COLLAGEN—*G. Strauss. Dissert. Abstr.* 1955, 15, 1510. *Via. J. Appl. Chem.* 6, 4, 579, (1956) : Measurements of heat of immersion (I) of collagen into water above and below shrinkage temp. were used to study its shrinkage and gelatinisation reactions in terms of the kind and no. of intramolecular bonds involved. I of native and shrunken collagen and of gelatin, into water, 2.90 M-NaCl and 2.70 M-MaSCN, over the temperature range 30°—80°, was measured. The results show that swelling, solution and shrinkage are all affected by internal cross-bonds, and are facilitated by (*a*) ions in solution which by their screening action weaken internal bonds and (*b*) ions or molecules (*e.g.*, SCN') which add on to polar groups on the protein and so break internal H bonds.

TESTING

STRUCTURAL ANALYSIS OF NOVOLAKS—*C. Boelhouwer, H. I. Waterman and P. H. W. Wijnands. J. Polym. Sci.,* 1955, 17, 411-415. *Via. J. Appl. Chem.* 6, 4, 605, (1956) : Novolaks were prepared by polycondensation of formaldehyde in acid solution, with phenol, and with p- and m-cresol, and subjected to hydrogenation at 300°/250 atm., using 100% (by weight) of a Ni/Cu catalyst. It is assumed that the mol. structure of the polymer has not been changed by this treatment. A study of the chemical constitution and physical properties of the resulting saturated hydrocarbons leads to the conclusion that these novolaks are linear thermoplasts and contain no " extra " rings. (13 references).

MODERN COMBUSTION FURNACES FOR ORGANIC ANALYSIS—*W. Zimmermann. Chem. Tech. Berlin*, 1955, 7, 595-598. *Via. J. Appl Chem.* **6**, 2, 236, (1956) : A discussion is given of modern apparatus for rapidly effecting micro and semi-micro combustion analysis of org. compounds by the Pregl method (for estimating C and H), the Dumas-Pregl method (in which C and N are first determined), and the Unterzaucher method (in which O is also estimated directly). Descriptions are given of typical commercial forms of apparatus, in which the combustion tube is heated evenly and rapidly, with close automatic control. Forms of heating used are gas burners automatically traversed along the combustion tube, and automatically controlled electric heaters. One form of the latter is detachable to enable rapid cooling of the tube. With these devices the time of combustion becomes a minor factor in the estimations.

ELECTROMETRIC TITRATION OF ZIRCONIUM—*Yu. I. Usaenko and G. E. Bekleshova. Ukr. khim. Zh.*, 1954, 20, 690-692. *Via. J. Appl. Chem.* **6**, 4, 525, (1956) : Zr is estimated by direct titration with NaF solution in presence of a little Fe^{III}, the end-point being indicated by the fall to zero of the Fe··· diffusion current between a rotating Pt electrode and a calomel half-cell. Al and Be interfere.

DETERMINATION OF ALUMINIUM—*A. K. Badko and T. I. Nazarchuk. Ukr. khim. Zh.*, 1954, 20, 678-683. *Via. J. Appl. Chem.* **6**, 4, 525, (1956) : A method is described for determining Al volumetrically pptg. it as Na^3AlF_6 and back-titrating the excess F_1 with standard $KAl(SO_4)_2$ in presence of alizarin as indicator. Fe interferes but can be separated by pptn. with $K_4Fe(CN)_6$ in presence of Zn ·· or Mn ··. The application of the method to the determination of Al in bauxite is described.

COLORIMETRY AND COLOUR GAMUTS—*T. Vickerstaff. Hexagon Dig.* 1955, *No.* 22, 13-21. *Via. J. Appl. Chem.* **6**, 4, 551, (1956) : The use of chromaticity diagrams based on the I.C.I. (Imperial Chemical Industries, Ltd.) primary colours, with particular reference to the matching of colours by dyers, is reviewed. Diagrams of the principal types of dyestuff are reproduced and discussed from this standpoint.

ANALYTICAL TECHNIQUE FOR SILICONE POLISHES—*L. Ivanovszky. Paint Manf.*, 1955, 25, 313-317. *Via. J. Appl. Chem.* **6**, 4, 574, (1956) : Two schemes are outlines for the analysis of water-free polishes. The procedures involve determination of solvent by steam distillation and abrasives by filtration after treatment with solvents. Waxes may then be determined by freezing of the filtrate and silicones by evaporation of the dewaxed filtrate. Alternatively, silicones may be mechanically separated from waxes after evaporation of the total sol. material. Another scheme is given for silicone emulsion polishes ; in addition to examination for components as above, tests for alkalis and emulsifying agents are included.

UREA ADDUCTS OF FATTY ACIDS. PART X. ESTIMATION OF THE ADULTERATION OF MUSTARD OIL WITH LINSEED AND GROUNDNUT OILS—*T. N. Mehta, B. Y. Rao, S. M. Abhyankar and B. H. Alase. J. Ind. Chem. Soc.* **19**, 1, 39, (1956) : The urea-adduct separation technique has been employed to estimate the adulteration in mustard oil with linseed and groundnut oils by concentrating the characteristic fatty acid, erucic acid. The % yield of C_{22} unsaturated acid in the adduct-forming fraction has been calculated from its iodine and neutralisation values to determine the percentages of mixed oils in mustard oil.

FABRICATION OF LEATHER

NEW LASTING MACHINERY—*Footwear, July* 1956 : A new and improved lasting machine is the " Thermalaster " for flat lasted types of footwear. This machine cements and lasts the upper to the innersole in one operation. A specially formulated adhesive for this work gives greater holding power and stands up under the heat from pounding, roughing and drying operations. Novel feed rolls make it possible to last around small radius curves at heel, toe and shank lines. Through the use of a manual adjustment, the operator can quickly change the strength of the machine's lasting-pull. A semi-automatic toe lasting machine has a single power control handle which raises or lowers the wiper carriage and advances or retracts the wipers. Having a 'bedding pressure' of over twelve hundred pounds, it produces a fine feather line and seals the adhesive bond firmly between lasting margin and innersole. Source : International Shoe Machinery Corpn.

BYE-PRODUCTS

DYEING OF WOOL WITH DIRECT DYES—*Philadelphia Section, AATCC. Amer. Dyest. Rep.* 1955, 44, 806-814. *Via. J. Appl. Chem.* **6**, 4, 587, (1956) : A comprehensive evaluation of some 260 direct dyes has been made, with particular reference to their dyeing performance (including light and wash fastness) on wool. From the light-fastness tests, a range of direct dyestuffs have been selected, which require 100 hours exposure before giving a break in the FadeOmeter. Wash-fastness with fabrics other than wool has also been tested. A detailed examination using certain selected dyestuffs was undertaken (exhaustion, dyeing rates, pH, electrolytes and auxiliaries), and a comparison with and milling dyes for both fastness and cost was made. Several direct dyes are worthy of serious consideration for wool dyeing ; their cost may be 20% lower than that of the milling dyes.

GENERAL

EFFECT OF STORAGE CONDITIONS ON THE PROPERTIES OF LATEX. I.—*H. M. Collier. I.R.I. Trans.*, 1955, 31, 166-173. *Via. J. Appl. Chem.* **6**, 4, 575, (1956) : Bulk shipments of NH_3-preserved latex

from Malaya exhibit loss of mechanical stability, though ageing for the same period in Malaya is well known to enhance stability. Co-operative testing of samples before and after shipment in bulk and in bottles has revealed the cause of stability loss to be exclusion of air. Loss can be prevented by allowing access of air or O_2. An increase in volatile fatty acid content occurs, in air-excluded conditions, which is much greater than that observed in aerated conditions.

THE ROLE OF INTERFACIAL ELECTRICAL CONDITIONS IN DETERGENCY—*K. Durham. J. Appl. Chem.* **6**, 4, 153, (1956) : A detergent system is treated as a lyophobic colloid system and the interaction between particulate soil and fibres in an electrolyte solution is represented by the superposition of the potentials due to London-van der Waals' attraction, the Born repulsion and double layer repulsion. The resultant potential energy curves are used to discuss the influence of electrical forces in soil removal and redeposition.

It is shown that the particle size of the soil, and the concentration and valency of electrolyte, are important parameters which determine the influence of interfacial electrical conditions in detergency. It is also shown that ease of soil removal is incompatible with a high degree of stability against redeposition. The relation between the surface potential (ψ_0) which is used in the theory to describe interfacial electrical conditions, and the zeta potential, derived from electrokinetic experiments, is discussed, and reasons for the lack of correlation between interfacial electrical conditions (described by zeta potentials) and detergent efficiency are given.

DEGRADATION OF NOVOLAK RESINS—*E. G. E. Hawkins. J. Appl. Chem.* **6**, 4, 131, (1956) : An attempt has been made to determine the structure of novolak resins by controlled degradation involving the steps : bromination, methylation of the phenolic groups, oxidation to polyketones, cleavage of the polyketones to bromoacids and bromoanisoles, demethylation and decarboxylation of the fragments, and analysis of the products. The method is applicable to simple novolaks, but the higher molecular weight compounds are incompletely cleaved to one-ring compounds.

EFFECT ON EMULSIONS OF THE HYDROXY-COMPOUNDS IN BEESWAX—*J. Pickthall. J. Soc. cosmet. Chem.* 1955, 6, 263-275. *Via. J. Appl. Chem.* **6**, 4, 574, (1956) : Tests comparing the emulsifying properties of untreated and acetylated beeswax showed that these properties depend to some extent on the presence of alcohols or other compounds containing OH-groups. It is considered that more attention should be paid to the acetyl value of beeswax in the analysis and general estimation of its properties.

SILICONE POLISHES—*J. A. Stapp.* (*Soap, N. Y.* 1955, 31, *No.* 9, 163-165, 195). *Via. J. Appl. Chem.* **6**, 1, 112, (1956) : The development and use of dimethyl silicone oils as ingredients in polishes, and some typical formulations of car and furniture polishes, are described.

PATENTS

COLLAGENOUS MATERIAL—*Ethicon Suture Laboratories, Inc.* (*B.P.* 731, 501, 5-8-53. *U.S.*, 8-8-52. *Via. J. Appl. Chem.* **6**, 3, 409, (1956): The connective tissue layers of mammalian gut, for surgical satures etc., after mechanical removal of fatty and non-collagenous proteins, are steeped in an aq. solution of the Na salt (I) of ethylenediaminepoly (tetra) acetic acid at $> 50°$ to remove substantially all remaining non-collagenous material. The strength of the solution may be 0.2 – 5 (0.3-2)% of I, temp. of steeping 20-40°, and period of steeping 7-18 hrs. The steeping solution may contain 5—10 wt.-% of a low-mol. Wt. aliphatic alcohol and/or a detergent. A further steeping in a fresh solution may be required, and this may be in a solution rendered alkaline to pH 8.0—11.5.

RECOVERY OF WOOL WAX FROM WOOL SCOUR LIQUOR FROTHS—*Commenwealth Scientific and Industrial Research Organisation.* (*B.P.* 729, 898, 24-11-53. *Austra.*, 2-12-52.) *Via. J. Appl. Chem.* **6**, 1, 111, (1956) : Froth produced from wool scour liquor (as a result of using non-ionic detergent, *e.g.*, a polyoxyethylene compound, or one of a sulphated high-mol. alcohol, during scouring) is treated with a dispersing agent, viz., Na or K phosphate, in presence of alkali (Na_2CO_3) if required (to give desired pH), to facilitate separation of wool wax. The latter may then be recovered by centrifuging, and purified by cooling, reheating, and centrifuging again.

STANDARDIZING AND MIXING COLOURS—*O. Syreeni. B.P.* 723, 965, 23-8-50. *Via. J. Appl. Chem.* **6**, 2, 250, (1956) : A basic colour substance (*e.g.* yellow) is mixed with amounts of two known standard basic colours (*e.g.* blue and red) to match a standard softening brown (or a standard grey colour mixture) in which the quantities of three basic colours (of equal intensity) are mixed in the ratio 1:1:1. Thus the huge and intensity of the unknown colour may be calculated and standardized colour can be built up by mixing the basic colours in the calculated proportions.

BOOK NOTICES

GAS CHROMATOGRAPHY—*The Chem. Age*, 74, 1927, 1334, (1956): In addition to descriptions of the various types of gas chromatography, i.e. gas-liquid partition, elution analysis and displacement analysis with gas-absorption chromatography, a good account is given of the theoretical

principles underlying the methods. A couple of chapters are devoted to experimental methods in which most of the important developments in technique are described in fair detail. The illustrations are numerous and of good quality and taken as a whole, the monograph represents a well-balanced and interesting account of the subject.

It will give an excellent idea of the scope of the methods to those, as yet unfamiliar, with the advantages to be gained from the employment of these new techniques. It is perhaps unfortunate, from the point of view of those who are about to use gas chromatography themselves, that so much space is wasted by the extensive divisions of the chapters into sections. There are no less than 51 sections in the 93 pages of text as well as a number of sub-headings. Space occupied by some of these headings could have been better employed for more detailed description of apparatus, or more discussion of methods and results.

Style is clear and readable, although a statement at the top of p. 17 ('as the pressure drops across the column approaches unity') is misleading. Another small point is that if it is considered of value to include the Greek word from which katharometer is derived (p. 39), it is important that the Greek should not be garbled. Price of the book seems high for its size although, no doubt, a substantial part of the cost is caused by the number of figures.

NOTES & NEWS

LEATHER SOFTENERS

A new line of concentrated leather softeners has been developed and factory tests have proven that the products contain high efficiency in application. One formula has been developed for black and leathers of dark colour which alleviates many lasting difficulties encountered in the more heavy and bony leathers. Where used it has practically eliminated upper damaged on hand lasting operations and does not dry the leather out hard when complete evaporation takes place.

Another formula is used for white and light and daintily coloured leathers. This is said to be fast to light and does not produce any after-yellowing effects.

Sources : C. F. Jameson Co. —*Footwear, July* 1956.

SHRINK RESISTANCE IN WOOL

Shrink resistance can be achieved in wool by removing or so modifying the scales of the fibre that the directional friction effect is lowered, and the friction equalised in both directions. In the past, this has mainly been done by acid chlorination, but this process has many disadvantages. The speed of the reaction makes absorption uneven : the solutions are difficult to handle, and special ventilation measures are required. The process in fact, is one of partial descaling, while even those scales that remain are loosened and tend to rub off in the wash. The fabric's "handle" becomes harsh, and there is a significant drop in weight.

None of these disadvantages occur with the Dylan process it is claimed. In this, the wool is treated with an alkaline mixture of permanganates and hypochlorites. No special equipment is required, and the process can quite easily be carried out by dyehouse operatives.

The scales are left intact, and wool treated by the process is said to be softer and whiter than untreated wool. Uniformity from batch to batch is readily achieved.

—*Fibres, Eng. & Chem.* **17**, 6, 197. (1956).

ATOM v. DEATH WATCH BEETLE

Atomic scientists in the United Kingdom are planning to use the atom to outwit the death watch beetle, which each year causes considerable damage to the woodwork of ancient buildings. Physicists at the atomic energy research establishment at Harwell, collaborating with timber experts, have found that small doses of radio-active cobalt can halt the reproductive instinct in the beetle and make its eggs infertile. The method they have developed will be used to protect historic buildings and furniture, the principal victims of this destructive insect.

—*The Chem. Age*, **74**, 1927, 1332. (1956).

LEADING SUPPLIER OF LEATHER

The following table shows the quantities and values of dressed leather imported into Malaya from various supplying countries during the year 1952, 1953 and 1954 :

(Quantity and value in '000)

	1952		1953		1954	
	Qty.	Value	Qty.	Value	Qty.	Value
	Cwts.	M $	Cwts.	M $	Cwts.	M $
Total imports	5	2,364	5	2,169	5	1,919
Of which from India	3	1,417	3	1,303	3	1,212
from Thailand		233	1	218	1	200
from Australia	0.5	283	0.5	240	0.6	297

It will be seen that India maintained her position as the leading supplier of this commodity to Malaya during the year 1954.

Principal items of exports from Malaya were petroleum products, tin, arecanuts, cocoanut oil, copra, rubber and palm oil.

—*J. Ind. & Trade*, **6**, 4, 469, (1956).

MARKETING OF LEATHER GOODS OF SOUTH

Mr. Bali, Assistant Manager, National Small Industries Corporation, Marketing Division, addressing the members of the Madras Chamber of Small Industries said that the Corporation was seriously considering the plans to take up the marketing of leather goods of the South through the Corporation.

He said the Corporation had already taken for marketing shoes from Agra, locks from Aligarh and Hoisery from Calcutta.

—*The Indian Express, dated 31st August* 1956.

C. L. R. I. NEWS

The Selection Committee for the appointment of technical personnel to the Institute interviewed candidates at the office of the Vice-Chancellor, Madras University on 27th August, 1956.

A meeting of the Scientific Advisory Committee of the Institute was held on the 5th September, 1956 under the Chairmanship of Shri Aggarwal, IFS, President of the Forest Research Institute and Colleges, Dehra Dun. In the absence of Prof. B. M. Das, Chairman, who could not attend the meeting on that day, Dr. Y. Nayudamma, Assistant Director, piloted the discussion.

Mr. John S. Dean American Glazed Kid Expert, joined this Institute in the month of August.

Mr. R. Selvarangan and Mr. J. C. Deb returned from the United States of America and Mr. J. B. Rao from United Kingdom after completion of the period of training.

VISITORS

Name	*Date of visit.*
Flt.-Lt. M. R. Gupta, Air Force, Tambaram ..	7—8—1956
Mr. Michael J. Dux, American Consul, Madras ..	10—8—1956
Mr. Frank S. Wilson, Industrial Development Adviser, U.S. Technical Co-operation Mission, New Delhi.	24—8—1956
The Viet-Namese Economic Delegation.	
Mr. Sitaram P. Pandit, Director, Western India Tanneries Ltd.	28—8—1956
Mr. H. A. Pilapil, Economic Affairs Officer, ECAFE, Bangkok, Thailand	31—8—1956

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