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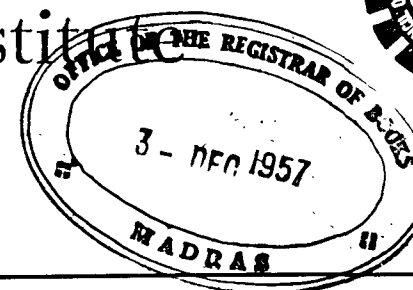
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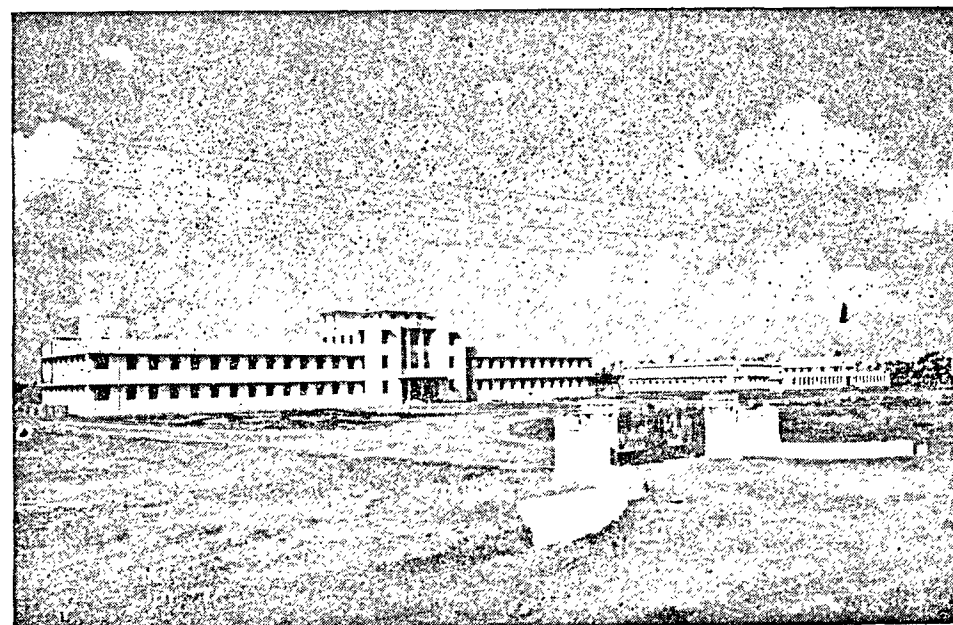


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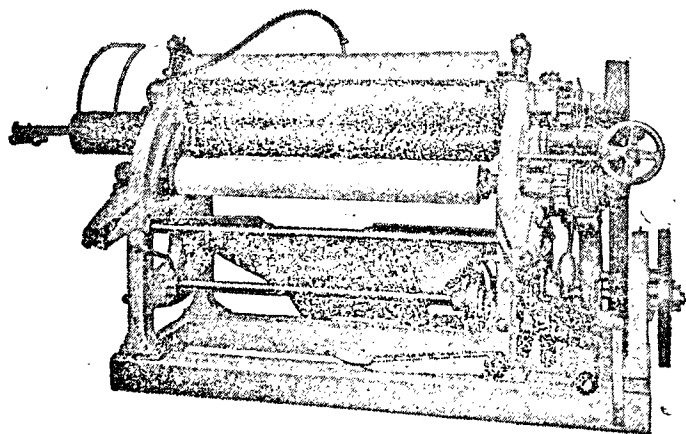
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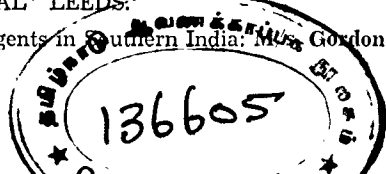
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SPECTROPHOTOMETRY IN LEATHER

RESEARCH: PART—VIII

Investigation of chrome complexes with inorganic acids and salts

D. RAMASWAMY & Y. NAYUDAMMA

SUMMARY

A u.v. Spectrophotometric method was applied to the study of the complex nature of the basic chrome solutions containing various inorganic acids and salts. The salts under study were sodium sulphate, sodium chloride, sodium sulphite, silicate, thiocyanate, fluoride and calgon. The absorbance data indicate that these inorganic ions may be grouped into three categories: (i) those having no effect on the penetration of the chrome complexes like sod. chloride, sulphate and silicate, (ii) those that give a maxima in the absorbance curve, namely sulphite and thiocyanate and (iii) those that produce a minima in the curve like calgon, sod. fluoride. The causes for the maxima and minima in the absorbance curves and the nature of chrome complexes formed are discussed.

The complexing nature of organic acids and their salts, with basic chromium sulphate solution was studied in the ultra-violet region, employing Molar ratio method and Job's method of continuous variations and the results reported earlier.^{1,2} In the present paper, the results on the study of the complexing nature of certain inorganic acids and their salts are reported. The acids and salts taken up for investigation are NaCl, Na₂SO₄, KF, Na₂SO₃, KCNS, sodium silicate, calgon, boric acid and phosphoric acids.

Experimental:

33½% basic chromium sulphate free from neutral salt was prepared by reducing Analar chromic acid with sulphur dioxide gas and basifying by the addition of calculated amount of barium hydroxide slurry filtering off the

barium sulphate and ageing the liquor for two months. Solutions of 1 molar acids and salts were prepared from Analar chemicals. Mixtures of solutions were prepared by adding the required amounts of acid or salt to 1 ml. of chrome liquor to give 1:1, 1:2 and 1:3 and 1:5 mole ratio of chromium to the added reagent and their absorbance readings taken with Model DU₄ Spectrophotometer after suitable dilution. By the continuous variation method x ml. of reagent adjusted to a pH of 4–4.2 were added to 1–x ml. of equimolar chrome liquor to give solutions differing in composition. The mixed liquors were heated to boiling point adjusted to constant pH of 3.2 to 3.3 and aged for a week continuing pH adjustment every day. They were made upto constant volume diluted and measured for their absorbance characteristics. The absorbance of the test solution after deducting the values due to the chrome and acid or salt alone was plotted against the molar ratio in one case and the composition of the liquor in the other case.

Data and Discussion :

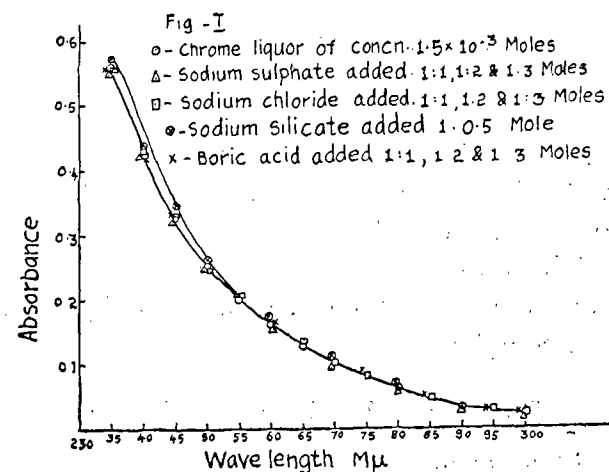
The data on addition of various moles of reagent to the same quantity of chrome could not be obtained with all the inorganic ions due to difficulties in precipitation, particularly at high molar ratios. Potassium fluoride precipitated at mole ratio beyond 1 of Cr. to 1 of KF, sodium silicate beyond 1 of Cr. to ½ of silicate, sulphite at 1:3 and beyond and calgon at lower mole ratios.

The curves obtained with sulphate, chloride, boric acid and silicate (1: ½ mole ratio only) are given in Fig. 1 which form into one group. It is seen from the figure that sulphate, chloride and boric acid did not cause any shift in the u-v. spectrum of chrome at all the mole ratios. These data are similar to the data obtained by Shuttleworth³ in his study on the effect of neutral salts in the visible region and indicate that these inorganic ions may not enter into the chrome complex at the concentrations employed.

The addition of silicate at lower mole ratio caused a slight shift in the range 235-245 mμ. However, not much of significance can be attached to this data since the shift is slight and the sample of silicate itself had some absorbance in this range. The precipitation of silicate at higher mole ratios could not be prevented even by adjustment of pH and addition of other electrolytes and hence no further data could be obtained on the silicate complexes of chrome.

Sulphite, thiocyanate addition :

Sulphite and thiocyanate constitute the next group, the curves of which as determined by Job's method are given in



Figs. 2 and 3 respectively. However, it has to be admitted in case of sulphite liquor that the absorbance readings went on changing during ageing and the data are of only comparative significance. The effect is perhaps due to the well-known unstable nature of the chrome sulphite complexes at room temperature and the decomposition of sulphite in acid solutions. It is clear from Fig. 2 that there is a well-defined maximum corresponding to 0.42 of Cr. : 0.58 of SO₃. On analysis, sod. sulphite was found to be only 87% pure indicating thereby that sulphite may form a complex corresponding to approximately 1:1 mole ratio. However, the curves particularly at lower wave-lengths have a profound shoulder

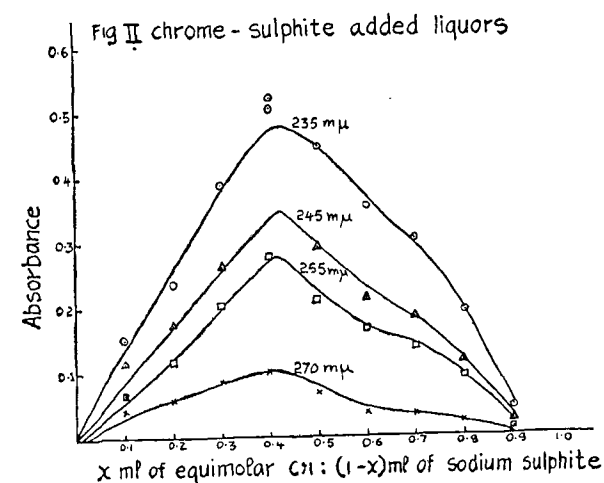
corresponding to mole ratio of 2 of chrome and one of sulphite which might also be simultaneously formed but possessing comparatively less absorbance than that of the 1:1 complex at the pH employed.

Fig. 3 shows that a maximum is obtained in case of thiocyanate added liquors corresponding to the composition of 0.5 denoting a complex of 1 chrome and 1 of thiocyanate. However the curve is not symmetrical on both the sides. Hence the simultaneous formation of other complexes, say for e.g., 2:1 cannot be ruled out. The thiocyanate ion may complex with chrome through nitrogen or sulphur.⁴ Figs. 2 and 3 showing the maxima indicate the newer types of chromium complexes formed by the addition of sulphite and thiocyanate to the basic chrome liquors. The anions like sulphite and thiocyanate might have penetrated in the chrome complexes by the displacement of either water molecules or sulphate radicals or the hydroxyl ions. The sulphite and thiocyanate might quite likely displace the water molecules and the sulphate radicals without disturbing the hydroxyl ion of the chrome complexes.

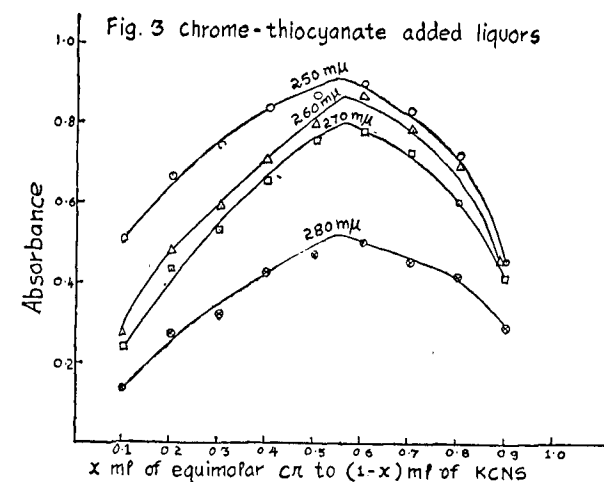
Fluoride and Calgon complexes :

Figs. 4 and 5 come as a contrast to Figs. 2 and 3. These relate to the complexing ability of fluoride and calgon with the basic chrome sulphate solution. As contrasted to the maxima obtained in the case of sulphite and thiocyanate, a definite minima is observed in both these cases. There is a certain amount of precipitation when calgon and fluoride are added to the basic chrome liquors. The difficulties of precipitation are overcome to a large extent by adding small amounts of dilute H_2SO_4 to the mixture. In spite of the precautions, the calgon precipitates basic chrome liquors when added in low concentrations. A significant trend, however, is that the absorbance values were negative for almost all the compositions with varied concentrations of calgon and

fluoride added to chrome resulting in a pronounced minima in the absorbance curve.



With the addition of potassium fluoride, there is a well-defined minima in the absorbance curve at the composition of 0.35 indicating the possibility of the presence of the chro-

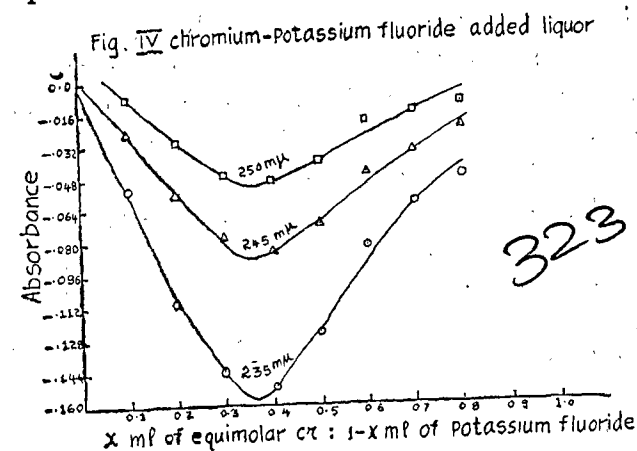


mium and fluoride in the mole ratio of 1:2. The values corresponding to 0.2 and 0.3 in Fig. 4 have to be considered with caution since absolute absorbance values for the mixtures at as low a wave-length as 230 mμ. were negligibly

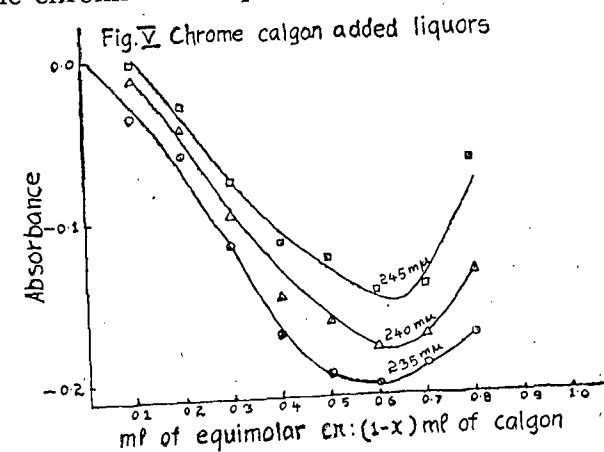
small. This pronounced minima in the absorbance curve might have resulted by the displacement of the hydroxyl ion of chrome complex by the fluoride ions. If hydroxyl group were to be totally displaced by fluoride ions, the ratio of the chrome to the fluoride should be 1:3 conforming to the formation of chromium fluoride whereas the absorbance curves indicate a ratio of 1:2 alone. The displacement of the hydroxyl ions by the fluoride was clearly indicated by the potentiometric and ion exchange and other studies conducted earlier in this laboratory.⁵ These earlier studies also clearly indicated that by the addition of fluoride, the cationic chrome sulphate is converted immediately into nonionic and anionic complexes. If the ratio of the chrome fluoride is to be retained as 1:2, as indicated by this particular study, it is quite likely that certain amount of hydroxyl ion is retained to form anionic or nonionic complexes. The minima observed may, therefore, relate to the nonionic or anionic hydroxyl fluoride complexes that might have formed.

Fig. 5 indicates the data for the chrome calgon complexes. Here again a minima is observed for the chrome complexes in the absorbance curves when the calgon is added to basic chrome solutions, though this minima corresponds roughly to two of chrome and one of calgon. The precipitation at low concentration of calgon and the formation of calgon-chrome complexes were indicated by earlier studies by potentiometric, ion exchange and other techniques.⁵ The results obtained here are in agreement with the earlier results. The calgon might displace the water, sulphate or hydroxyl radicals of the chrome salt. Calgon is similar to fluoride in showing the characteristic minima instead of maxima as contrasted to sulphite addition. This may mean that calgon may displace the hydroxyl ions of the chrome complexes and may form nonionic and anionic complexes. The ion exchange studies conducted earlier show that the calgon forms nonionic and anionic complexes with the addition of the increasing amounts of calgon, unlike fluoride.

These studies further indicated that calgon is different from fluoride ion as the formation of these nonionic and anionic complexes is gradual and not immediate as in case of fluoride. The addition of potassium dihydrogen phosphate and pyrophosphate in the place of calgon did not show any de-



finite trends due to difficulties in precipitation. Addition of phosphoric acid, however, resulted in negative differential values and probably due to displacement of OH groups from the basic chromium compounds or deolation.



It is, however, premature to attempt the elucidation of the structure of these inorganic complexes. Further work is in progress in this direction.

These results, however clearly point out that certain inorganic acids and salts have no complexing effect. These are sodium sulphate, sodium chloride and sodium silicate and boric acid. Certain inorganic ions do complex with the basic chrome sulphate. This may be classified into two categories, one resulting in positive absorbance curves and the other resulting in negative absorbance values with a striking minima in the curves. Sod. sulphite and thiocyanate form the former group and the fluoride and calgon ions form the latter group. The differences in the absorbance values may be attributed to the differences in the complexing ability of these inorganic ions and the mode of complexing of these ions with the chrome complexes as well as to the differences in the nature of the charges on the complexes so formed. It is quite likely that the sulphite and thiocyanate may penetrate into the chrome complexes by the displacement of water molecules and acid radicals whereas calgon and fluoride may not only displace water and acid radicals but also the basic hydroxyl radicals resulting again in nonionic and anionic complexes. Sufficient data is, however, not available to elucidate the structure. Further work is in progress to confirm these findings.

Chemistry and Physics Division,
22-7-1957.

REFERENCES

1. Ramaswamy, D., J. Lea. Tech. Assn. India, 4, 2, 51, 1956.
2. Ramaswamy, D. & Nayudamma, Y., J.A.L.C.A., 52, 67, 1957.
3. Shuttleworth, S. G., J.S.L.T.C., 34, 410, 1950.
4. Zhdanov, G. S., & Zvonkova, Z. V., Doklady, Meshdurarod Kongr. Teorch, i. priklad, Khim. XIII, Kong. Stockholm 1952, 135-74. Cf. C.A., 48, 6304, 1954.
5. Nayudamma, Y. & Selvarangan, R., Bull. C.L.R.I., 2, 4, 118, 1955.

EFFECT OF ACID AND SALT ADJUSTMENT IN E.I. TANNAGE WITH PELTOPHORUM FERRUGINEUM BARK

M. K. UDAYA VARMA · E. C. MATHEW & (LATE)

B. M. DAS

SUMMARY

E. I. tanning experiments using Peltophorum ferrugineum bark have been carried out with various quantities of sodium sulphate, sodium formate and sodium lactate. Sodium sulphate and sodium lactate effect improvement in colour. Since stiffness of the leather is increased by all the three salts, the addition of these salts does not seem to be beneficial for E. I. kip tannage with Peltophorum bark. However, as sodium lactate gives greater firmness, this addition may be useful for sole leather tannage using this bark.

Peltophorum ferrugineum bark when used alone produces a light coloured, full and strong leather of desirable feel very similar to the E.I. tanned kips.¹ Experiments were conducted to find whether the tanning properties of this bark could be further improved by suitable adjustment of Acids and Salts.

Experimental: The butt portion of a wet salted cow hide was limed and delimed as for E.I. tanning and pieces of approximately 7" × 3" were cut for the experiments. The pelt was divided in such a way as to avoid discrepancies in results due to pelt variations. Liquor prepared by leaching Peltophorum bark overnight was adjusted to 18°Bk. 750cc. of this liquor having a pH of 4.7 were taken in each of ten battery jars. Weights approximately corresponding to the following equivalents of salts were added to the liquors and well stirred.

Expt.	I: No salt added.
"	II: 30 mgm. equivalent of sodium sulphate per litre.
"	III: 100 " "
"	IV: 150 " "
"	V: 25 mgm. equivalent of sodium formate per litre.
"	VI: 80 " "
"	VII: 120 " "
"	VIII: 25 mgm. equivalent of sodium lactate per litre.
"	IX: 60 " "
"	X: 120 " "

TABLE I

Analysis of the liquors at the commencement of Tanning

	I	II	III	IV	V	VI	VII	VIII	IX	X
Tannins (gms./l.)	22.38	22.38	22.38	22.38	22.38	22.38	22.38	22.38	22.38	22.38
Non-tans (-do-)	18.9	18.9	18.9	18.9	18.9	18.9	18.9	18.9	18.9	18.9
° Bk	18	18	18	18	18	18	18	18	18	18
pH	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7
Free acid (to pH 5.8) (mgm. eq./l.)	14.0	15.04	15.84	15.84	17.72	21.84	25.2	15.44	17.72	20.12
Total salt (sulphated ash method) mgm. eq./l.	54.8	85.2	144.6	202.8	79.7	135.7	190.9	78.9	116	174
Salts of weak acids (titration to pH 2.0) mg. eq./l.	13.9	15.9	35.7	51.6	55.6	107.3	146.9	47.9	91.3	139
Salts of strong acids (Total salts-salts of weak acids)	40.9	69.3	108.9	151.2	24.1	28.4	44.0	31.0	24.7	35.0

TABLE II

Analysis of liquors after Tannage

	I	II	III	IV	V	VI	VII	VIII	IX	X
Tannins (gm/l)	1.68	1.18	1.168	0.829	1.465	2.898	3.608	2.48	2.275	3.567
Nontans (-do-)	17.54	21.96	31.68	38.08	21.09	28.89	33.4	22.75	28.31	34.43
pH	5.4	5.5	5.6	5.6	5.7	6.0	6.4	5.85	6.0	6.1
Free acid (to pH 5.8) mgm. eq./l.	4.91	2.1	2.9	4.5	1.64					
Total salts (sulphated ash method) mgm. eq./l.	44.04	76.95	117.7	182.7	95.96	125.6	167.2	82.26	117	149
Salts of weak acids (titration to pH 2.0) mgm. eq./l.	30.96	42.87	59.54	73.84	71.47	116.7	150.1	74.4	107.2	138.1
Salts of strong acids (Total salts-salts of weak acids)	13.08	34.08	57.16	108.86	24.49	8.9	17.1	7.86	9.8	10.9

It was found that the addition of these salts did not alter the pH values of the liquor appreciably. They were brought back to the original value vis. pH 4.7 by the addition of lactic acid. The free acid, total salts and salts of weak acids in the liquors were determined (Table I) and the pelt put in. The liquor pelt ratio was 7:1. Pelts were handled daily and examined on the second, fourth and ninth days for penetration, feel and colour. The tanning was complete in 20 days. They were bleached with a solution containing Perfect Tan O and Oxalic acid (2:1) and then put in myrobalan liquor of 20°BK. On the 22nd day, they were oiled with ground nut oil and dried. The liquors after tannage were analysed (Table II).

Observations after tanning for :

- I. 24 hours. The pelts were uniformly coloured and were rather firm. Pelts in experiments 2 and 3 were firmer than the others.

Penetration :

Expt.	I	2 units
"	II	1 "
"	III	2 "
"	IV	1½ "
"	V	1½ "
"	VI	1 "
"	VII	2½ "
"	VIII	1½ "
"	IX	1½ "
"	X	1½ "

II. After 72 hours :

	Penetration	Feel
Expt. I	Almost complete	Soft
" II	¾ penetrated	Soft
" III	Only a thin line of un-penetrated portion	Firmer than above.
" IV	Almost complete	Firm
" V	-do-	-do-
" VI	¾th penetration	Firmer than above.
" VII	¾th "	Not as firm as above.
" VIII	¾ penetration	Not very firm.
" IX	¾th "	-do-
" X	¾th "	Firmer than above

III. After 8 days :

	Penetration	Feel	Colour
Expt. I	Complete	Firm	Light
" II	A very thin streak of un-tanned portion	-do-	Lighter
" III	Thin streak of untanned portion	Softer than above	-do-
" IV	-do-	Firm	-do-
" V	Almost complete	Soft	light
" VI	-do-	-do-	lighter
" VII	Thin streak of untanned portion	-do-	-do-
" VIII	-do-	-do-	light
" IX	-do- near flesh side	-do-	very light and uniform
" X	-do-	-do-	light

Chemical analysis of all the leathers were done and the results are given in Table III.

A comparison of the experimental leathers with the control is given in Table IV.

Discussion

Sodium sulphate series: The addition of sodium sulphate to the tanliquor has retarded the penetration of tanning in all experiments. But it improves the colour and plumps up the leather. The more the addition of sodium sulphate the better is the colour but plumpness is reduced by greater amounts of sodium sulphate though in all cases plumpness is more than that of the control. The yield is not appreciably affected by the addition of this salt. The leather becomes stiffer and the tensile strength is increased. This increase is proportional to the amount of salt added. The degree of tannage is lowered progressively as more and more of salt is added. The water soluble matter in the leathers for which salt has been used is lower. The shrinkage temperature is raised.

Sodium formate series: Sodium formate also retards the penetration of tannins in all the experiments. It increases the plumpness and stiffness of the leather. Tensile

strength is also appreciably increased. The leather is patchy. Though the addition of 25 mgm. eqvts. have lightened the colour, the addition of larger quantities of formate darkens it. The yield of leather is increased in all cases. The degree of tannage of all the leathers is lower than that of the control. The water soluble matter is not affected by the addition of 25 mgm. eqvts. of salt but it is lowered by further addition of salt. Shrinkage temperature is raised.

Sodium Lactate Series: Sodium lactate has also retarded the penetration of tannin in all experiments. The use of this salt improves the colour. The addition of 25 and 60 mgm. eqvts. of sodium lactate have made the leather non-patchy and has produced the lightest colour. The firmness increases with the increase in quantity of this salt. The addition of 120 mgm. eqvts. makes the leather very stiff and hence this addition may be useful in sole leather tannage. Tensile strength is also appreciably increased. In this case also, water soluble matter is not affected by the addition of 25 mgm. eqvts. of salt but is lowered by further additions. The yield is not appreciably affected.

Comparison of the effect of these different salts shows that sodium sulphate effects the least improvement in colour. Formate and lactate improve the colour better but the leather becomes patchy. Plumpness of leather is the greatest when 20 mgm. eqvts. of sodium sulphate is added. 120 mgm. eqvts. per litre of sodium lactate also produces a plump leather. It is noted that in all experiments the penetration of tannin into the hide is lowered by the presence of salts. This is contrary to the general concept that salts assist the penetration of tannin. Nayudamma et.al.² have shown that "salts of hydroxy acids do not help the rate of penetration of tannin when they are used either for the pretreatment of the pelt or liquor"; "...Certain inorganic salts impede the penetration." While the results of experiment using sodium sulphate and sodium lactate are in agreement with

TABLE III

	I	II	III	IV	V	VI	VII	VIII	IX	X
Moisture	14.16	13.79	14.13	13.51	13.72	14.09	13.87	14.02	13.05	12.37
Oils & Fats	3.07	3.08	3.42	3.51	3.38	3.61	3.91	4.56	4.16	5.02
Total ash	0.72	0.66	0.7	0.66	0.84	0.69	0.72	0.82	0.88	1.15
Soluble ash	0.53	0.5	0.3	0.3	0.3	0.3	0.54	0.74	0.14	0.22
Insoluble ash	0.19	0.16	0.4	0.33	0.54	0.39	0.18	0.08	0.74	0.93
Water soluble matter	6.11	5.5	5.3	5.26	4.79	5.13	6.39	6.22	5.45	6.05
Hide substance	45.85	48.08	48.13	49.18	48.39	48.27	45.87	47.13	48.63	46.71
Fixed tans	30.62	29.39	28.62	28.21	29.18	28.51	29.78	27.99	27.97	28.92
Degree of tannage	66.77	61.13	59.47	57.36	60.32	59.07	64.92	59.39	57.51	61.91
pH of water solubles	3.65	3.75	4.5	4.45	4.55	4.5	4.9	5.35	4.55	4.3
Shrinkage temperature °C.	76	78	79	79.5	78	78	78	76	76	77
Colour of leather — Y	3.1	3.1	3.0	3.0	3.0	3.5	3.0	2.5	3.0	2.0
— R	2.5	2.0	2.0	2.5	2.5	2.0	2.0	2.0	1.5	2.0
Tensile strength (lbs./sq. in.)	3930	4434	4535	5522	5328	5589	5223	5738	6049	5459
Yield %	54.1	54.6	54.8	54.9	57.2	56.5	57.1	54.5	53.7	56.4

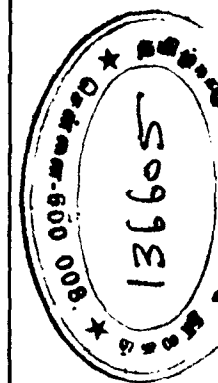


TABLE IV

	Genl. appearance	Colour	Feel	Crack at single fold	Tearing Strength	Leather quality	Remarks
I. No salt added (Control)	Good	Good	Soft	No.	No.	Strong	Good plump leather.
II. 30 mgm. eq. Sod. sulphate	Good	Better	Somewhat stiff.	No.	No.	Strong	Good plumper leather.
III. 100 mgm. eq. Sod. sulphate	Good	Better than No. I.	Slightly stiffer than I, but softer than II.	No.	No.	Strong	Good leather but less plump than II; plumper than I.
IV. 150 mgm. eq. Sod. sulphate	V. good	"	Stiffer than I to III.	No.	No.	Strong	Good leather. Plumper than I; but less plumper than II & III.
V. 25 mgm. eq. sod. formate	Good	Better than I.	Slightly stiffer than I.	No.	No.	Strong	Good plump leather.
VI. 80 mgm. eq. sod. formate	Patchy	Lighter than I, but slightly darker than V.	Stiffer than I & V.	No.	Slight	Strong	Not good
VII. 120 mgm. eq. sod. formate	Patchy	Darker than V & VI, almost same as I.	Stiff.	No.	No.	Strong	Not good
VIII. 25 mgm. eq. sod. lactate	Patchy	Lighter than I.	Stiffer than I.	No.	No.	Strong	Slightly plumper than I.
IX. 60 mgm. eq. sod. lactate	Patchy	Same as above.	Stiffer than VIII.	No.	No.	Strong	Same as above.
X. 120 mgm. eq. sod. lactate	Good	Lightest	Very stiff.	No.	Crack	Strong	Plump leather of good appearance.

these findings the penetration in the formate series is at variance with the observation that sodium formate increases penetration. All the experimental leathers are firmer than the control. Okell³ has stated that increase in the total free acid produces a firmer leather. So the firmness in these experimental leathers may be due to the increase in free acid content of the liquor brought about by small quantities of lactic acid added to adjust the pH. Cheshire's⁴ findings are also similar, i.e., "The presence of much acid brings about increased firmness in the leather." Asbye and Rasmussen (Stiasny Festchrift 1939,9)⁵ have noted that lactic acid gave greater firmness to leather.

Chemistry & Physics Division,
8-4-1957

REFERENCES

1. Udaya Varma, M. K., Mathew, E. C., & Das, B. M. *Bull. C. L. R. I.* 2, 7, 209 (1956).
2. Nayudamma, Y., Jayaraman, K. S., & Krishnan, T. S. *Ibid.*, 3, 4, 150, (1956).
3. Laurance Okell, R. *J. I. S. L. T. C.*, 29, 59, (1945).
4. Cheshire, A. *Ibid.*, 24, 143, (1940).
5. Cheshire, A. *Ibid.*, 24, 133, (1940).

TECHNICAL SEMINAR

Seminar on Physico-chemical investigations of
Tannin Fraction of Babul*

Y. NAYUDAMMA

Babul is one of the indigenous and important tanning materials which is widely used for sole leather tannage. Freshly cut babul bark was extracted with ethyl acetate after removing chlorophyll, gums and fats by treatment with chloroform methanol and petroleum ether. From ethyl acetate soluble fraction, the ether soluble fraction was obtained by extraction with dry ether. The ether soluble fraction was further fractionated by precipitation with benzene. The methyl and acetyl derivatives of all the fractions were prepared. All the fractions and their derivatives were studied by various physico chemical techniques. Chromatographic studies revealed some definite spots with the ether soluble fractions. Electrophoretic studies indicated one fast moving constituent towards anode probably associated with the carboxyl group of the tanning material. By employing photometric and non-aqueous titration techniques, it has been found possible to differentially titrate and thereby determine the acidity due to the carboxyl groups and due to activated and total phenolic groups. The u-v spectra of all the fractions and their derivatives have been taken and they throw light on the mixed character (pyrogallol and catechol) of all the fractions. The shifts in the maximum absorption on addition of aluminium chloride and buffer may also probably be attributed to the same effect. With the acetylated fractions, it is possible to determine the percentage acetylated by various techniques.

The whole study has brought to light the important role played by the various physico-chemical techniques in the characterisation and study on the nature of the vegetable tannin fractions.

* Paper read at the Seminar held on 26th July, 1957.

CLASSIFIED ABSTRACTS

RAW MATERIALS

DAMAGE IN SALTED HIDES. E. Raabe. *Przeglad Skorzany*, 1956, No. 2, 35: *Polish Tech. Abstr.*, 1956, No. 4, 119. Via. *J.S.L.T.C.*, 41, 5, 184 (1957).—The harmful effects of magnesium and calcium salts in curing salts are emphasised, and limits for such impurities are given. Suitable additions to salt are mentioned.

DISINFECTION OF HIDES FROM DISEASED ANIMALS. E. Niepokojczka. *Przeglad Skorzany*, 1956, No. 4, 5: *Polish Tech. Abstr.*, 1956, No. 4, 123. Via. *J.S.L.T.C.*, 41, 5, 184, (1957).—Mercuric chloride treatment was favoured, as 0.05% solution inhibits the growth of sporulating organisms. The Seymour-Jones method (formic acid and mercuric chloride) tended to give hardened edges to the hide. Other treatments such as o-phenylphenol, p-dichlorobenzene, and KCNS with HCl were either too weak in disinfecting properties, or affected the character of the hide.

PROCESSES PRIOR TO TANNING

PRACTICAL BATING. THE EFFECT OF BATING VARIABLES ON SIDE AND CALF RESEARCH QUALITIES. Robert Stubbings, *J.A.L.C.A.*, 52, 6, 298 (1957). Results of practical bating trials in six tanneries are reported. The tests were made on full-scale production lots, and the results are reported in terms of effects on individual properties of the leather such as break, temper, drawn grain, etc. Variables studied include quantity and type of enzyme, temperature and time of bating, and deliming conditions. The results obtained in the different tanneries are in excellent agreement.

TANNING

VEGETABLE TANNING

KAHUA BARK IN SOLE-LEATHER MANUFACTURE. P. V. R. K. Reddy, K. A. Joseph and K. Padmanabhan, *Ind. Com.*

J., 12, 2, 118 (1957).—Kahua (*Terminalia arjuna*) bark, which can be repeatedly cut as the bark grows again and again in three year rotation basis, contains both catechol and pyrogallol tannins and the tannin content varies from 16 to 23 per cent. Practical tanning trials with this bark alone to produce sole leather gave leathers of reddish colour and the analysis of these leathers gave low degree of tannage. But when a blend of 50% kahua and 50% myrobalans was used, leathers of good colour having high degree of tannage (81.00) were obtained.

K. S. R.

FORMATION OF RESINOUS, GUMMY SUBSTANCES IN SUMAC EXTRACTS BY ALTERATION OF THE NON-TANNINS. A. Yague Gil, Bol. Asoc. Quim. Espan. Ind. Cuero., 15, 35-42, (1954), Via J.A.L.C.A., 52, 6, 352 (1957).—The author makes a careful study of the variations of the composition of sumac extracts obtained and treated under different conditions (aqueous alcohol or water extractions, detannization, etc.). He finds that in an extraction with aqueous alcohol (1:1) the relation T/NT is higher than in a water extraction, with a much smaller amount of sugars and an absence of resins and gallic acid, and also a smaller alteration of the solutions. The nontannins form resinous, gummy substances which are known to be formed from the sugars. Hides tanned with an aqueous alcohol extract were of normal aspect, whereas hides tanned with a water extract, rich in sugars and containing gallic acid, were firm and showed a much darker color.

INFLUENCE OF VARIOUS FACTORS IN THE EXTRACTION OF OAKWOOD TANNINS. M. Zurakowski and W. Wisniewski, Przegląd Skorzany 1954, No. 10, 17; Polish Tech. Abstr. 1955, No. 2, 145, Via J.S.L.T.C. 41, 5, 185 (1957).—For industrial extraction, the wood should be reduced to pieces of less than 0.5 cm., and for thicker shavings, time or temp. should be increased. The optimum extraction temp. is 97°, and the maximum extraction time per diffuser should not exceed 2 hr. If pressure extracted, the pressure was satisfactory at between 1-2 atmos., and extract yield decreased at 3 atmos., and a temp. of about 135° C.

CHROME TANNING

BUFFERS IN CHROME TANNING. B. Krassowski, Przegląd Skorzany, 1955, No. 5, 102; Polish Tech. Abstr., 1956,

No. 2, 139, Via J.S.L.T.C., 41, 5, 185 (1957).—The use of sodium nitrite and sodium sulphite for reducing the acidity of the liquor during tanning is described. Sodium nitrite can be used without displacing any of the previously added masking salts.

OTHER TANNAGES

INFLUENCE OF SOME ORGANIC ACIDS IN THE SOLUTION OF BASIC ZIRCONIUM SULFATES. M. Pierre Porter and M. Henri Martin, Bull. Assoc. Fran. Chem. Ind. Cuir. 18, 4, 71, (1956).—Study on the effects of adding various organic acids to basic zirconium sulfate, Zt. 45 (Fabrican Chemical Products) containing sodium sulfate, ZrO_2 24%, schorlemmer basicity about 45% is made. By the addition of various amounts of acetic, lactic and formic acids, the pH of precipitation increases with the increase of the ratio of acid/ ZrO_2 in the case of acetic and lactic acids where as it is less pronounced in the case of formic acid. Similar results were observed with salts of these acids. Electron migration studies revealed that in the mere ZT 45 containing sodium bisulphite, the migration commences from pH 3.0, the pH of precipitation, beyond which the formation of non-ionic complexes are indicated. With the addition of acetic acid and lactic acids in the pH range 2-7, it is mainly anionic and its migration towards anode is less marked and at around pH 4.5-5.0 it seems to have predominance of non-charge complexes. In the case of Zr. oxychloride, the migration is towards cathode between pH 2-7. The increasing order of complexing ability can be arranged as CO''_3 , $HCOO'$,

CH_3COO' , $CH_3CHOHCOO'$, $\begin{matrix} COO \\ | \\ COO \end{matrix}$. From the observed data, the probable structures for the complexes are also presented.

K. S. R.

STUDIES ON THE DIFFUSION OF BASIC SULFATES OF ZIRCONIUM IN THE GELATIN. M. Pierre Porter, B.A.F.C.I.C., 19, 2, 31, (1957).—The relative influence of organic acids on the rate of penetration of zirconium in leather (see also above Abst.) was studied by measuring the diffusion of salt in the gelatin. To study the diffusion, a series of graduated tubes, half filled with a warm aq. sol. of gelatin 15% pure, containing alizarine sulfonate of soda are taken. After cooling, gelatin formed gel consistant. The penetration of the Zirconium was visualised by the change of colouration of the yellow alizarine to a red lake in mild acid.

Variation of the rate of diffusion of tanning solutions as a function of quantity of organic acids presented were studied and the observations made in the course of different projections were summarised thus:

1. The zirconium content in a solution of basic sulfate of zirconium diffuses very rapidly into a gel of gelatin when added to lactic acid solution.

2. With a solution of basic sulfate, all pass together through that partition of miscelle formation to zone of feeble concentration in zirconium as if there was massive fixation of zirconium to the surface of gel and ultra-filtration.

3. The rate of diffusion of zirconium augmented with the concentration of ZrO_2 in the solution.

4. In the presence of lactic acid, the zone of diffusion of the Zr. is more homogenous.

5. The acetic and lactic acids enable to obtain solutions diffusing in an important way at pHs superior over pH of flocculation with normal basic sulfates.

6. The presence of 0.5 mol. of lactic acid per molecule of ZrO_2 is sufficient for obtaining homogenous diffusion of the Zr. in the gel of gelatin.

Further, when the comparative studies were made with gel of zirconium and the solutions containing acid, the acid diffused more rapidly than zirconium. In the case of chrome the sulphuric acid diffused more than Cr_2O_3 .

K. S. R.

THE EFFECT OF ALUMINIUM SULPHATE AND POLY-VALENT METALS ON THE VISCOSITY OF GELATIN SOLUTIONS. A. Kragh, *J.S.F.A.*, 3, 6, 351 (1957).—Trivalent metals give a viscosity maximum at different pH values. Chromium differs from other metals like aluminium, iron and zirconium in that there was no viscosity increase. In the viscosity pH curve the maximum occurs at pH 4.3 for aluminium sulphate addition. It is suggested that at pH 3 particularly hydrated aluminium oxide is obtained which forms electro-static links with ionised carboxyl groups of gelatin. As the amount of this oxide increases with the increase in pH, there is a sharp increase in viscosity. As the pH is further increased the aluminium salt is more fully hydrated and

does not form cross links and decreases the viscosity. This is a reversible effect followed by an irreversible change leading to the precipitation of colloidal suspension. The fully hydrated oxide reaction of other metals like Iron, Zirconium and Chromium, are in many respects analogous. In the case of chromium, however, a co-valent bond is formed.

Y. N.

CHAMOIS LEATHER MANUFACTURE. *L.T.R.* 124, 3714, 443 (1957).—To remove the natural grease reliming after splitting is preferred to solvent processes. The pickled goods must be depickled overnight raising the pH to 8 with Borax and then relime. Emulsifying agents containing cyclic groups will retard and inhibit oxidation. The recent trend is to use Degras and synthetic Degras as emulsifying agents. The excess alkali neutralises the free acids in the oils and thus retards oxidation. The pH of the pelt during stoving should be between 4 and 4.5. Oxidation preceedes most evenly in weakly acidic conditions. The difficulty in stripping off excess oil after stoving may be due to incomplete penetration of the oil, leading to excess polymerisation. The best condition is to use just sufficient oil to give complete penetration, say, 30 to 40% on the weight of the goods; and to strip the goods immediately they are considered leathered. The colour of the leather depends upon the type and quantity of oil and the rate of stoving. Deep colour is obtained from dark viscous oil with iodine values generally give slowing up the rate of oxidation all tend to give a darker colour. The use of formaldehyde tends to give a pale yellow colour.

Y. N.

CONTRIBUTION TO THE STUDY OF SILICA TANNING. P. Chambard and R. Lassarre. *Bol. Asoc. Quim. Espan. Ind. Cuero*, 15, 54-61 (1954) *Via J.A.L.C.A.* 52, 6, 351 (1957).—The subject is treated under the following aspects: (1) history; (2) tanning properties of the acid sols of silica in relation to their stability, concentration, and pH; (3) effects of the fixation of the silica (blockage of certain reactive groups of collagen); (4) trial of combined tannages with silica and vegetable or mineral tanning agents (Cr, Fe, Zr, polymetaphosphate); (5) possible reactions between the

silica sol and the skin, and theory of silica tannage. A sol of a diluted solution of Na_2SiO_3 in a mixture of conc. HCl and acetic acid containing 2.5% SiO_2 was used. For maximum fixation, it is necessary to use a concentration of 15% SiO_2 on lime-weight basis, but the maximum fixable percentage of SiO_2 is almost reached from a concentration of 10%. The speed and percentage of fixation of this tannage are between those of the vegetable and chrome tannages. Best results were obtained with these sols when they were 48 hr. old, and with a pH of 2.6-3.2. Tests with deaminated skins showed a very slight decrease of the percentage of fixed SiO_2 , which proves that the fixation of silica does not take place with the free amino groups only; other combinations can take place.

SULPHITE CELLULOSE WASTE LIQUOR. W. Abramowicz and W. Sarnecki. *Prace Inst. Celuloz—Papiernm*, 1954 No. 1, pp. p. *Polish Tech. Abstr.* 1955, No. 4, 129 *Via J.S.L.T.C.*, 41, 5, 185 (1957). By dialysis two fractions of lignosulphonic acid can be isolated, each have different compositions and properties. The dialysed fraction contains 35% and the undialysed fraction 65% of the waste liquor solids. That part of the liquor which can be salted out with NaCl shows, by comparison with other fractions isolated by combined dialysis and salting-out, the highest content of tanning substances (83%). This part of the liquor is almost entirely contained in its undialysed fraction. The lowest content of tanning substances (28%) was found in the dialysed fraction of the waste liquor. The content of tanning substance in the solids of the non-fractionated liquor was 47%.

PROCESSES AFTER TANNING

PREFERENCE FOR ANIONICS. Frank J. Chadwick. *Lea. & Shoes*, 133, 3, 12, (1957).—Tanners are again showing preference for the anionics for fatliquoring most types of leathers. Simplicity to handle, capability of functioning in a wide temperature range and forming emulsions in live steam or even at boil and the ease with which the blending with other anionics or with insoluble materials is accomplished are the strong features for their preference. Too much adjustment of the fatliquoring oils has been asked for rather than some modification in leather preparation. Amount of float, neutralisation and pH of the leather surface have a pronounced effect on emulsion behaviour. Many tanners favour the idea of controlling penetration of the oil particle by regulating the pH of

the leather surface at the time of oil addition. The oil industry put forward a new anionic in the form of a solubilized Moellon which produces a very fine particle size emulsion and more stable to the action of electrolytes than the sulphated oils. It is showing promise as an additive in regular chrome tannage and vegetable or resin retans. Other developments in this direction are described in brief.

K. S. R.

CHROME TANNING AND FATLIQUORING. C. E. Retzsch. *Lea. & Shoes*, 133, 3, 13 (1957).—In early 40's, Nopco Chem. Corp. was asked to develop an oil that would be stable in the presence of alum and salt for direct fatliquoring of alum tanned skins instead of using blend of raw oils, egg yoke, flour, gums, clays etc. Such a product was discovered and it was found that this product could be used in tanning bath to bring about simultaneous tanning and fatliquoring operations. The product was used in the making of alum tanned baseball, lace and welting leather. Later, the demand for the water resistant leather led this firm to approach on the problem further. The water resistance could be imparted by adding the proper materials at a later stage in the retanning operation. The success of this procedure led to the extension of this method to chrome leather. In other types of leather, the use of suitable oil in the chrome tan bath followed by a normal fatliquoring operation produced a very soft, supple leather at the same time saving labour and time. In addition, it had been found that the use of oil in tanning bath resulted in a fuller leather having greater tensile strength.

K. S. R.

NONIONIC AND CATIONIC APPLICATIONS. Dominic Meo. *Lea. & Shoes*, 133, 3, 14, (1957).—The advantages and disadvantages of nonionic and cationic emulsions are reviewed.

K. S. R.

DYEING AND FINISHING SUEDE LEATHER WITH POLISH DYES. J. Turski, M. Kajzer, R. Dobosz, and S. Przybys. *Przeglad Skorzany*, 1954 No. 7, 1: *Polish Tech. Abstr.* 1955 No. 2, 97, *Via J.S.L.T.C.*, 41, 5, 184 (1957).—Excessive preliminary fat-

liquoring is undesirable for uniform and thorough colouring. The most satisfactory temp. was 35°C with certain acid, direct and basic Polish dyes. A levelling agent was also used. Dark brown shades were obtained by double-bath dyeing. Egg yolk was the best fat-liquoring medium.

REDUCING THE CONSUMPTION OF CHROME LEATHER BLACK IN LEATHER DYEING. *Przegląd Skorzany*, 1954, No. 10, 225. *Polish Tech. Abstr.* 1955, No. 2, 147. *Via J.S.L.T.C.* 41, 5, 186, (1957).—Suitable proportions of sodium thiosulphate and sodium carbonate were used with a chrome black (Polish M. extra quality) to effect a saving of about 10% of dyestuff.

THEORIES

THE STRUCTURE OF ALPHA-KERATIN. *Maurice L. Huggins. Proce. National Acad. Scs., of U.S.A.*, 43, 2, 204 (1957).—A new model structure is suggested to avoid the difficulties that arose due to the assumption of α Keratin structure to consist of helices of 13 atom-ring type, in a close packed arrangements.

K. S. R.

THE STRUCTURE OF COLLAGEN. *Maurice L. Huggins, Proce., National Acad. Scs., of U.S.A.*, 43, 2, 209 (1957).—Structure of Collagen involving 3-chain coiled coils proposed by Rich and Crick and Ramachandran though avoids some difficulties of the earlier models, does not explain certain principles such as formation of hydrogen bonds wherever possible and tendency of like groups to be surrounded by close neighbours and also the large extensions (7 or 8 fold) of the band pattern observed in electron microscopic pictures. The structure proposed earlier by the author (*J. Am. C. Soc.* 76, 4045, 1954) though agrees with X-ray data, gives maximum hydrogen bonding, permits about 3½ fold extension etc., but has the serious disadvantage that half the CO.NH groups have *cis* transformation which seems to be in contradiction to the infra red evidence. The new structure proposed now has only *trans* orientation of CO.NH groups and seems satisfactory from other points of view such as X-ray, analytical, infra red data and electron microscopic pictures.

K. S. R.

CONTRIBUTIONS TO THE DETERMINATION OF THE ISOELECTRIC POINT OF COLLAGEN. *A Staib. Bol. Asoc. Quim. Espan. Ind. Cuero*, 16, 79-88, (1954) *Via J.A.L.C.A.*, 52, 6, 349 (1957).—This paper is based on Loeb's work, which proved that the potential difference between a protein sol in a collodion bag and the exterior liquid media is zero. The eletrosmosis method is used to confirm the results. Measurements were made when collagen was added to acid and alkaline solutions, and to the same solutions plus NaCl. The influence of swelling agents, as well as that of tannage, was also studied. A full description of the method, as well as tables and graphs of the results, is given. The author concludes that at the I.P. the collagen and medium are isoionic for H⁺, which indicates that the I.P. depends on the dissociation constants of the acid and the collagen salt. The NaCl moves the I.P. to the acid side. The I.P. of collagen presents different values, depending on the nature of the swelling of the protein, and it is not a constant that defines its purity. The I.P. indicates a physico-chemical state of the protein. Its determination is very important, as it reveals the modifications introduced in the disposition of the protein macromolecule, and permits the identification of the functions of a chemical compound. It also reveals the state of the collagen in the unhairing and tanning operations, which constitutes another control method of regulating the quality of the product.

TESTING

A TENTATIVE SIMPLIFIED METHOD FOR THE ANALYSIS OF LIGNINSULFONATES. *P. A. Dentsch and W. R. Kenzie, J.A.L.C.A.*, 52, 6, 312 (1957).—The ALCA Method for tannin analysis is not suitable for ligninsulfonates because of the slow rate of reaction of the latter with hide powder. An alternative method is described in which the attainment of conditions of equilibrium is greatly hastened. It consists essentially in mixing a portion of specially prepared, air-dry hide powder with a small volume of relatively concentrated sample and after a short absorption period, shaking with a known volume of water and determining the unabsorbed nontannins. Analytical figures are given for a number of ligninsulfonate tanning materials and vegetable tannins. Small variations in the pH of the analytical solution have a marked effect. The method shows promise as a simple and convenient technique for ligninsulfonate analysis.

ULTRAVIOLET PHOTOMETRIC METHODS OF TANNIN ESTIMATION IN RELATION TO WATTLE EXTRACT UTILIZATION. D. G. Roux, *J.A.L.C.A.*, 52, 6, 319 (1957).—The ultraviolet photometric method of tanning estimation, based on an absorption maximum at 280 m μ (1), was recently shown to be highly correlated with the hide powder method for black wattle extracts (2) and was used to investigate the official method (3). An alternative ultraviolet method based on absorption maximum in the far ultraviolet ($\lambda_{\text{max.}} = 203 \text{ m}\mu$) is described, and its relationship with the hide powder and existing photometric procedures ($\lambda_{\text{max.}} = 280 \text{ m}\mu$) is assessed. Attention is drawn to the accuracy and applicability of photometric methods as elegant research tools and rapid estimation methods in leather chemistry.

PAPER CHROMATOGRAPHIC ANALYSIS OF THE NAPHTHIONIC SYNTAN. Arnaldo N. Roseira, *J.A.L.C.A.* 52, 6, 330, (1957).—Conditions for chromatographic examination of naphthalene syntans have been studied, including choice of paper, solvent phase, and developing agent. Basic dyes, particularly Methyl Violet 2 B, are suitable developing agents. Examples of chromatograms of commercial syntans are given, and a possible application of the chromatographic procedure is suggested.

THE ANALYSIS OF HAIR TINTS. I. Jacobelli-turi. *Rendiconti 1st Super. Sanita, Roma*, 19 461-69 (1956). Via *J.A.L.C.A.*, 52, 6, 347 (1947).—The proposed methods may be used not only for hair tints but also for research in the field of fur dyes. The dyes may be detected chromatographically, and in this first report the data are given for several commonly used compounds. The values of R_f were determined by examining the chromatographic spots obtained using as solvent a 4:1:5 mixture of butanol, acetic acid, and water at 20°C. The R_f values are: p-phenylenediamine, 0.38; 2,5-toluylenediamine, 0.48; p-aminophenol, 0.55; pyrogallol, 0.71; resorcinol, 0.83. As it may happen that several other compounds have R_f values very close to those indicated above e.g., pyrocatechol, R_f 0.82, several color reagents were studied which may be used to identify the single constituents: (a) saturated (cold) aqueous solution of vanillin containing HCl (2.5 ml. per 100); (b) 0.5 g. of o-dimethylaminobenzaldehyde and 30 ml. HCl in 100 ml. H₂O; (c) 1 g. phenol in 100 ml. of 5% KOH containing 20 ml. of a dilute solution of Na hypochlorite; (d) 1 drop aniline in 250 ml. H₂O acidified with 10 ml. acetic acid and 3g. Na persulfate; (e) 1% solution of

silver nitrate. The sensitivity of these reagents permits the detection of the above indicated compounds at concentration of 0.2-0.5% per ml.

DETERMINATION OF BASICITY OF CHROME LIQUORS. W. Lask and B. Krassowski. *Przeglad Skorzany*, 1954, No. 4, 5. *Polish Tech. Abstr.*, 1955, No. 1, 139, Via *J.S.L.T.C.*, 41, 5, 184 (1957).—The indirect method and Stiasny's method have been compared against (a) a solution of pure chrome alum (b) an SO₂-reduced solution of K₂Cr₂O₇ basicity 33%, and (c) an SO₃-reduced liquor masked with either sodium oxalate or sodium formate.

MASKING NUMBER AS AN INDEX FOR VALUATION OF ORIGINALLY REDUCED CHROME LIQUORS. W. Lasek. *Przeglad Skorzany*, 1954, No. 11, 2436 *Polish Tech. Abstr.*, 1955, No. 2, 97, Via *J.S.L.T.C.*, 41, 5, 184 (1957).—The masking number (ratio, expressed as a percentage, of the number of g. equiv. of the masking substance contained in the liquor to the total g. equiv. of Cr) can be expressed by the formula $M = Z_{\text{theor.}} - Z_{\text{analyt.}}$, where $Z_{\text{theor.}}$ (theoretical basicity of reduced liquor) is computed from analytical results of the chrome liquor prior to reduction, $Z_{\text{analyt.}}$ (analytical basicity of reduced liquor) is determined by the indirect method. A knowledge of the masking number assists in standardising production, and helps in the investigations of the formation of organic acids during organic reduction of the Cr^{VI} salts.

TESTING OF DYESTUFFS AND LEATHER: B. Niewieczeral. *Przeglad Skorzany*, 1954, No. 9, 199; *Polish Tech. Abstr.* 1955, No. 2, 147. Via *J.S.L.T.C.* 41, 5, 184 (1957).—A description of methods used in Poland and elsewhere for testing dyestuffs and fastness of dyed leathers. Methods are reviewed for fastness to light, rubbing, water, fat-liquoring, perspiration and formaldehyde. Careful solution of the dyestuff is necessary to prevent staining, and a method is given for testing the solubility of dyestuffs.

GENERAL

STUDIES ON CASTOR OIL. HYDROGENATION OF CASTOR OIL. Srinivasan, Kamath and Kane, *J.A.O.C.S.* 34, 302 (1957).—Products of low iodine value 10 and hydroxyl value, 35-40 can be readily obtained by hydrogenating Castor Oil at atmospheric pressure and at temperatures of the order of 220°, using 1% Raney nickel. Dehydration of ricinoleic acid and subsequent hydrogenation

of the resultant double bond as also simple saturation of ricinoleic acid are the main reactions occurring during hydrogenation. When hydrogenation is carried out at room temperature, under a pressure of 40 p.s.i. with alcohol as solvent, a product rich in monohydroxy stearic acid is obtained.

Y. N.

A STUDY OF THE MECHANISM OF FATTY SPUE FORMATION II. R. G. Mitton and K. G. A. Pankhurst. *J.S.L.T.C.* 41, 5, 161 (1957).—There would appear to be at least two stages in the formation of fatty spue on leather: (1) the migration of fat from the centre to the grain surface, and (2) the crystallisation of the fat on the surface in the form of a large number of minute crystals. It is quite possible that progressive crystallisation of fats on the surface may, in itself, provide part of the motive force causing the fat to migrate from the interior.

In the work described, the presence of dyes, mordants, and detergents is shown to have a marked influence on the formation of fatty spue, as well as such physical factors as the thermal history of the leather, the presence of crystallisation promoters (seed crystals), and mechanical action. Whether the dyes, mordants, and detergents act merely through their effect on crystal growth, or whether they set up a concentration gradient from the centre to the surface cannot be decided from the evidence available. Oleic acid cannot be used successfully as a crystallisation inhibitor.

THE ASPERGILLI OCCURRING IN TANNERY. THEIR ACTIONS. J. Boidin and J. Prevot. *Bull. Assoc. Fran. Chem. Ind. Cuir.* 19, 2, 47 (1957).—The work done on *Aspergillus* occurring in tannery in various countries is reviewed. Systematic notion and classification of *Aspergillus* are outlined. Qualitative and quantitative studies were made on the action of the different species of *Aspergillus* on tannins, proteins and the glycerides and on tanned leathers. *A. flavus* is found more dangerous owing to its multiple attack on tannins, fatty materials and leathers. *A. niger* is particularly active on tannins which explains its frequent occurrence on the liquors of coloured suspenders. More over its pigmentation marked leathers very dull. *A. fumigatus* and *A. ochraceus* have shown non-negligible aggressivity. The activity is found to be reduced sufficiently

for *A. unguis* and nil from species of groups *glaucus*, just like *A. candidus* and *A. versicolor*. The species more aggressive are effectively those which occur more frequently on leather.

K.S.R.

MICRO-ORGANISMS AND THEIR RELATIONSHIP TO TANNING OPERATIONS. Edward F. Weiss. *The Lea. Manfr.*, 74, 4, 21 (1957).—The history of the micro-organisms in general, their existence, development, destructive and constructive activities are reviewed. The types of micro-organisms, the conditions for their development and the modes of their operation at various stages of leather processing and storage which cause monetary loss and means to control them are discussed.

K.S.R.

BOOK NOTICES

REVIEW. THE CHEMISTRY OF TANNING PROCESSES. K. A. Gustavson. *Academic Press Inc. New York*, 1956, pp. 403 72s net; Post 1s. 6d. Through *J.S.L.T.C.* 41, 5, 188 (1957).—This valuable addition to the small number of competent text-books on tanning chemistry should receive the widest welcome, not least because of the author's eminence in this field of study, and the high personal regard in which he is held by all those who know him. Gustavson's contribution to the subject cover a period of over thirty years and there can scarcely have been a more prolific writer on a wider range of tanning problems. With such a background of experience and thought to draw on, it is not surprising that he has produced a book that is both stimulating and provocative.

The author disarms criticism by confessing that he is writing from a personal point of view, and that he expects disagreement with this viewpoint. It seems likely enough that this will be forthcoming, and the controversies of recent years in which he has been involved will not be ameliorated by the pungent criticisms which recur throughout the book, often as almost casual asides. There is no harm in hard cut and thrust between scholars in any subject, provided it is borne in mind that in a subject where, to use the author's words, "knowledge of reactions... is scanty, evidence is contradictory, and speculations are rife", dogmatism is not justified, and over and over again he warns the reader against too facile con-

clusions on incomplete evidence—a warning which everyone familiar with the intricacies of the subject will heartily endorse.

Of the ten chapters in the book, four are devoted to chromium salts and chrome tanning, and these are undoubtedly the best. The discussion on chrome complexes is probably as complete as can be found in the literature anywhere, and should be of permanent value to workers in this particular field outside the leather industry; it is probably true to say that the work of leather chemists, and Stiasny and Gustavson in particular, represents a major contribution to pure science. These chapters reflect Gustavson's long devotion to chrome tanning, but nevertheless, it is somewhat disappointing to find that, by comparison, the space he devotes to vegetable tanning (one chapter) is much less, and the reason he gives for this, is that the former is more important economically and has been more thoroughly investigated, will not meet with universal agreement. There is no reference, for example, to the work of the Beverley school and absorption theories in general receive scant treatment in spite of the fact that there has been a marked revival of interest in them during the last fifteen years.

The remaining chapters deal with aldehyde, quinone and oil, and combination tannages; the aldehyde chapter is particularly complete. The final chapter extends the subject beyond the immediate sphere of leather manufacture into the biological and medical field, and references to phagocytosis, for example, and the work of Gordon and Thompson, recall the tradition of collaboration that exists between the Leather Department and the Medical School at Leeds that is symbolic of the mutual interests of two widely separated fields of study.

The author expresses the hope that his book will stimulate enquiry, and he need have no fear that it won't, numerous lines for further research are implied throughout, and the immense growth of our knowledge of collagen alone necessitates a reappraisal of much of the work up to the war period. The fact that collagen is dealt with separately and at length in a monograph by the same author, published concurrently with this volume, has provided leather chemists with an almost complete summary, stimulating and controversial, of the many theories and the supporting evidence, of the processes of tanning.

NOTES & NEWS

PSYCHROMETRIC DIFFERENCE CONTROL. *L. T. R.* 124, 3709, 232 (1957). A new drying control unit which was developed by the B.L.M.R.A., was exhibited on the stand of the Directorate of Scientific and Industrial Research at the Instruments, Electronics and Automation Exhibition at Olympia during May, 1957. The unit is to control the drying capacity of air to a drying unit by supplying only just sufficient heat to ambient air to maintain a constant psychrometric depression. The main control consists of two chrome plate and thermometer bulbs (liquid expansion) connected by capillary tubing to a compensatory linkage mechanism so that the movement of a pointer is governed by the difference in temperature between the bulbs and not by the actual temperature. One bulb is fitted with a sock kept wet with distilled water by a constant level irrigator. An increase in the temperature difference between the wet and dry bulbs causes the pointer to move towards a preset needle carrying electrical contacts. On making contact in electrical relay system actuates a magnetic valve, thus cutting off the supply of steam or hot water to the drying plant. For certain products it is essential that the temperature does not exceed a certain figure regardless of the rate of drying. A thermostatic control is therefore linked into the same circuit to override the wet and dry bulb difference control should the temperature exceed a preset figure.

SOLE LEATHER SOLD BY AREA. *L. T. R.* 124, 3709, 235 (1953). Footwear sole leather is now being sold by area instead of by weight by Melrose Tanners of Beverley, Yorks. In recent years, technological progress has introduced the chrome retan process for sole leather. Compared with this new process, orthodox vegetable tanning produces a sole leather which is rather rigid and which has been sold by weight. The use of the chrome retan process or combination vegetable and mineral tanning, however, has enabled the production of a flexible sole leather without impairing its wearing qualities. Such chrome retanned sole leather can be readily measured in the standard machine which has been used for some decades past to sell flexible upper leather by

the foot. Melrose Tanners had for several months now been selling its combination tanned sole leather by the foot. It believes that such a method provides a more reliable yardstick for both manufacturer and shoe repairers and states that selling by area has already been well received.

AMERICAN "PIGS-KIN" FURNITURE TILES. L.T.R. 124, 3710, 280, (1957). The Kilfer Tanning Company in the United States has recently designed and developed entirely new type furniture tiles called Genuine "Pigs-kin" leather tiles. "Pigs-kin" tiles combine the mellow beauty and resiliency of natural leather with the durability found in other fine materials. They are impregnated with a combination of durable finishes which laboratory tests show are highly resistant to abrasion, heat, acid, alcohol and stains. They have excellent recovery against indentation and are easily cleaned and polished. The new furniture tiles require only the usual dusting and waxing given to all fine furniture. In case a tile is damaged, it is easily replaced. Standard size tiles are 4½ inch square and 4½ inch by 9 inch.

PATTERN CARD FOR CIBA POLYCOR RANGE. L.T.R. 124, 3710, 289 (1957). Good all round fastness and suitability for various types of leather are the principal advantages claimed by Ciba Limited for Polycor dyes, a range of anionic dyestuffs, in their newly published pattern card, No. 2825/57. The pattern card, a substantial and well-produced volume with card-binding, contains specimens of two shades each in yellow, orange, light brown, brown, dark-brown, red blue, dark blue, grey and black and of one shade each in green, dark green, Bordeaux and violet. All the colours are demonstrated as samples of full chrome grain calf, full chrome suede calf, chrome retanned gloving leather, vegetable tanned E.I. goatskins and vegetable tanned split hides. The range of colours is expendable in combining one with another. Particular tables are included for all the specimens in the book, showing fastness to light, acid and alkali, water, washing, perspiration, formaldehyde and buffing, and there are also ratings for solubility and penetration.

C. L. R. I. NEWS

Symposium on "Leather Auxiliaries"

The Indian leather industry fetches to the Indian Union Rs. 400 million annually. Presently over Rs. 80 million worth of skins are exported in the raw form and about Rs. 200 million worth are exported in the semi-tanned or unfinished form. If these raw and semi-tanned materials could be finished and finished leathers and leather goods exported, the value of the Indian leather industry will be doubled, if not trebled.

A variety of materials like sharpening agents, deliming and bating materials, synthetic, vegetable and other tanning agents, oils and oil products, dyes, finishes, lacquers, adhesives, shoe polishes, etc., under the name of leather auxiliaries go into the tanning and finishing of leathers and leather goods. At present a large amount of leather auxiliaries are being imported into India at great cost valued at about Rs. 20 million annually. The finished leather industry has not been well developed in India because of the lack of technical know-how and lack of supply of these leather auxiliaries. The leather auxiliary industry in Western countries conducts research on its own and contributes a good deal to the development of newer products and processes for leather tanning and finishing. It is to provide the technical know-how to the leather industry, the Central Leather Research Institute was established in the year 1953. During these four years of its existence, this Institute has been able to command the confidence of the Indian Tanning Industry and the technical know-how in regard to the manufacture of a variety of leathers has been provided to the Industry. With the availability of the technical know-how and the interest shown by the Indian tanner to produce finished leathers and leather goods, the demand for these leather auxiliaries is ever increasing. It is urgent and imperative that necessary arrangements should be made in India to provide the Indian tanner with the required leather auxiliaries. Dependence of the Indian industry on imported materials is undesirable, particularly in view of the present drive for saving in foreign exchange.

The number of auxiliary products that go into leather-making are many but the quantity consumed for each is small. The manufacture of these products may be undertaken on a small as well as large scale. In some cases like dyes, these could be made with profit only on a large scale. In some cases, the bye-products of a major industry may be conveniently converted into leather auxiliaries. To meet the growing demands of the leather industry and to save foreign exchange, a joint venture of foreign firms with the Indian firms may prove very fruitful. The symposium may prove to be a meeting ground for the Indian tanner, the foreign manufacturers and the dealer to discuss these problems and to derive first-hand knowledge about the scope of setting up such industries either individually or under joint ventures. It is sincerely hoped that many of the foreign firms would be able to send their technical representatives to focuss the latest trends in their products.

Recognising the important role played by the leather auxiliaries in the rapid development of Indian leather industry, a symposium is being organised at the Central Leather Research Institute towards the end of December 1957. At this time, the Conference of Indian Chemical Engineers and the Indian Science Congress will also take place in Madras. This will give the visiting scientists and technologists from India and abroad an opportunity to attend these various conferences concurrently with this symposium to be held at the Central Leather Research Institute.

The subjects to be presented at the symposium are classified in Appendix A. The papers may be presented either in English or in any other language. An advance copy together with an abstract of the paper to be presented at the symposium may kindly be forwarded before 30th November 1957 to enable us to finalise the programme and to circulate the abstracts of the papers. Arrangements will also be made for getting the papers read and discussed in the case of absentee authors.

Those who are interested in participating in the symposium are requested to fill in the enclosed form (Appendix B) and return the same on or before 30th November 1957.

In connection with the symposium, an exhibition of leathers, leather goods and leather auxiliaries will be organised at this Institute. You are requested to make this exhibition a success by sending exhibits.

Along with the exhibition, the Central Leather Research Institute will have an "Open House" for a period of one week. This gives the general public an opportunity to go round the Institute and see the exhibitions as well as the work being done at this Institute. One can see the raw materials, processing methods, experimental and testing techniques, charts and models and the finished products. The research workers will show you the work being done and explain how and why the work at this Institute is important to the leather industry and the country.

Arrangements will also be made for the delegates to visit some of the tanneries and places of interest in and around Madras City.

It is hoped that you and the members of your organisation will be able to attend the symposium and present papers which would offer an opportunity of establishing personal contacts and enable exchange of ideas for the development of the Industry.

An early reply will facilitate drawing up of a detailed programme which is to follow.

APPENDIX—A

LEATHER AUXILIARIES

Scope

- I.
 1. Curing Agents.
 2. Soaking Agents.
 3. Depilants.
 4. Deliming agents.
 5. Bating and Puering materials.
 6. Pickling materials.
- II. *Tanning: Vegetable Tanning:*
 1. Natural tanning materials.
 2. Tanning extracts.
 3. Modifiers.
- III. *Mineral Tanning Agents:*
 1. Mineral Tanning agents :
- IV. *Other Tanning Agents :*
 1. Syntans.
 2. Oils-Synthetic and natural.
 3. Aldehydes.
 4. Combination tannages.
 5. Miscellaneous tannages, viz., silica, sulphur, calgon, sulphite, cellulose, etc.
- V. Neutralising, Stripping, Clearing and Bleaching Agents.
- VI. Surface Active Agents.
- VII.
 1. Oils, fats and waxes.
 2. Water-proofing materials.
- VIII. *Finishing Materials :*
 1. Mordants.
 2. Dyestuffs.
 3. Binders : Natural and Synthetic.

4. Pigments.
 5. Formulation of leather finishes.
 6. Water and lacquer finishes.
 7. Enamel finishes.
- IX. Leather dressings.
 - X. Filling agents, adulterants & their substitutes.
 - XI. Evaluation, testing, standardisation, marketing, imports, exports, production, etc.
 - XII. Adhesives.
 - XIII. Disinfectants, fungicides.
 - XIV. Miscellaneous.

APPENDIX—B

CENTRAL LEATHER RESEARCH INSTITUTE MADRAS-20

Particulars to be supplied by those wishing to participate in the symposium.

1. NAME.
2. FULL ADDRESS.
3. (a) Title of paper.
(b) whether the paper deals with fundamental or applied aspects, or is a review.
4. Do you intend to take part in the general discussions on the subjects.
5. If so, please indicate title and send a short abstract.
6. Is accommodation in Madras to be reserved for you.
7. Are you interested in visiting tanneries in and around Madras.
8. Any other request or suggestion not covered above.

PRACTICAL DEMONSTRATIONS

The practical demonstration No. 7 on the 'Manufacture of E.I. Kips and Skins' was conducted at this Institute during the

month of August 1957. The following tanners' representatives attended the demonstration.

1. Mr. A. Anwar Basha, Messrs M. Quayim & Co., Tannery, Melvisharam, N.A. Dt.
2. Mr. B. S. Venkataraman, Messrs. E. K. M. & Sons, Erode.
3. Mr. K. Abdul Rahim, Messrs. E. K. M. & Sons, Erode.
4. Mr. Berisai Bhagat, Government Tannery, Gumla, Ranchi (Bihar).
5. Mr. Sree Ramachandar, 1-Satnagar, Karol Bagh, New Delhi.
6. Mr. T. H. Abdul Majid, Messrs. T. A. Latif & Co., Ambur.
7. Mr. M. P. Abdul Kudoss, c/o Mr. M. K. Shaik Mohideen, Ponganur, Tiruchirapalli.
8. Mr. S. Gulmohamed, Ramjinagar, Tiruchirapalli.
9. Mr. P. Abdul Gafoor, Messrs. P. M. Batcha & Co., Periamet, Madras-3.
10. Mr. C. Hafzur Rahman, Messrs. C. Abdul Subhan Abdul Samad & Co., Tannery, Pernambut.
11. Mr. C. Sadulla Basha, Messrs. S. H. Fazur Rahman & Bros., Tannery, Pernambut.
12. Mr. C. Anusahmed, c/o A. Hajee Mohamed, Tannery, Pernambut.
13. Mr. M. A. Mohamed Aiyob, Messrs. Perna Hajee Abdul Kayoom & Sons, Tannery, Pernambut.
14. Mr. P. E. M. Krishnan, Tanner, C. T., Ltd., 78, C.P. Koil Street, Madras-14.

The Practical Demonstration No. 8 on the 'Dressing of E.I. Kins and skins using Basic Aluminium Sulphate was started on 16th September 1957.

Hon'ble Sri Morarji Desai, Union Minister for Commerce and Industry, visited the Central Leather Research Institute on Friday, the 23rd August, 1957. He was taken round the laboratories and tannery and shown the important research projects that are under investigation and completed. Inaugurating the Export Promotion Committee on the same day Sri Morarji Desai referred to his visit to the Leather Institute earlier in the day. He said they used to send out raw materials without processing

them. They come back as finished goods and they paid more for them. They must find a process whereby goods could be processed here. Some people complained that the Leather Institute was competing with local businessmen and manufacturers. He wished to point out that the Research Laboratory attached to the Institute had to give them advice which would be acceptable. The advice would be acceptable only if its value was demonstrated.

At the reception given at Hotel Connemara by the Southern India Skin and Hide Merchants' Association on the 23rd August, 1957, referring to the plea for allowing the import of wattle bark, the Union Minister said that at least three to four varieties of bark had been made available as good substitutes by the research laboratories here and suggested that they should learn to make the best use of the available substitutes for tanning purposes.

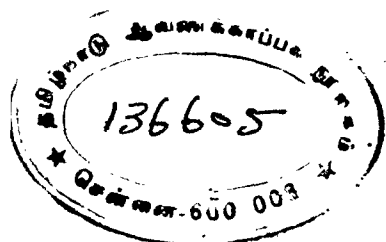
Mr. P. S. Venkatachalam, Junior Scientific Officer, Central Leather Research Institute, Madras, who has been awarded a Scholarship under the Colombo Plan had left for U.K. on the 24th August 1957 to receive training in 'Leather Dressing' at the Leather Sellers College and in other 'Leather Dressing' factories of the U.K.

Dr. Y. Nayudamma, Assistant Director-in-charge, Central Leather Research Institute, Madras, has been nominated as Member of the newly formed Export Promotion Advisory Board for the Southern Region.

Dr. Y. Nayudamma, Assistant Director-in-Charge, Central Leather Research Institute, Madras, attended the meeting of the Southern Regional Committee on Animal Husbandry convened at Trivandrum by the Indian Council of Agricultural Research from 28th August to 31st August 1957.

VISITORS

Name	Date of visit.
Students of Wesley High School, Madras-14	9-9-1957
Lt. Col. C. N. Hussain, Superintendent, T.D.E.L., Kanpur	9-9-1957
Mr. James W. Stott, Messrs. Pickers (Private) Ltd., Ahmedabad	10-9-1957
Shri Chandulal S. Shah, President, Leather goods Manufacturers' Association, Bombay	13-9-1957



ERRATA

Vol. III, No. 11, June 1957.

Page 419. Footnote. Read "tanners" for "farmers".

" 422, line 12. Read "Paranitrophenol" for "Paranitrophemol".

" " line 19. Read "Fish oil 6%%" for "Fish oil 66%%".

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Page 16, line 14. Read "partly accounts for" for "partly for".

" 23, " 23. Read "titration" for "titation".

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