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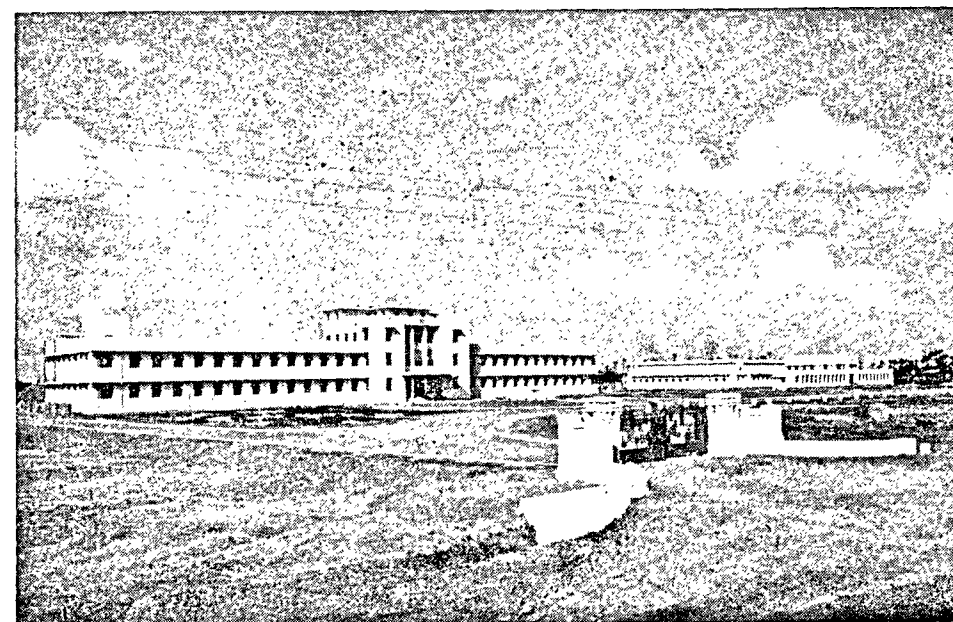


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Vol. III JULY, 1957 No. 12

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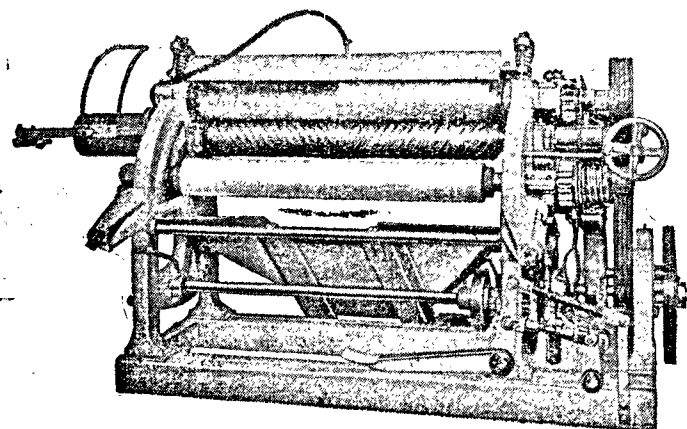
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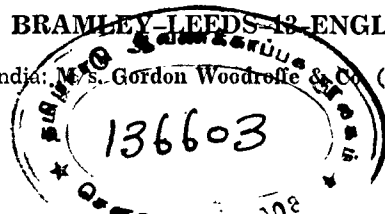
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COMBINATION TANNAGES : PART V

Combination Chrome Vegetable Tanning in Single Bath *

T. S. RANGANATHAN & Y. NAYUDAMMA

SUMMARY

The factors that govern the fixation of chrome by hide powder tanning with veg-chrome liquors like the concentration, pH, effect of neutral salts like sodium chloride and oxalate and the nature of chrome complex fixed in the tanned hide powder have been studied. The results further confirm that veg-chrome liquor imparts the characteristics of both chrome and vegetable tan to the leathers tanned with it.

The preparation of chrome-vegetable tanning liquors and the chemical composition of the constituents of the same have been discussed in the earlier paper.¹ The organic acids produced during the reduction and the presence of some organic degradation products of tannin of varying sizes were expected to give some special characteristics to the leathers tanned with such liquors. Results obtained on such a study are reported in this paper.

Tanning experiments with hide powder: In all experiments, 15 grams of the standard hide powder were taken, transferred to a 400 cc. bottle, exactly 140 cc. of distilled water added and shaken in a mechanical shaker for two hours. Then the required amount of the tanning liquor was added, keeping the total float constant in all the cases by the addition of the required amount of water. The tanning was carried out for 24 hours in the shaker, taken out, squeezed well and then washed well thrice successively with 350 cc. of distilled water (each wash 4 hour) to remove all the water soluble matter. After this, the powder was squeezed well, the lumps were broken down and dried in

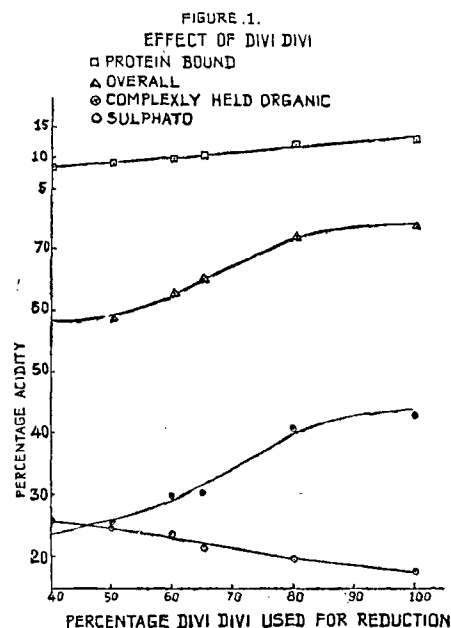
* Forms part of thesis for the M.Sc., degree of the Madras University.

air at room temperature. When dry, the powder was thoroughly mixed and taken for analysis.

In tanning with the different liquors prepared, the same percentage of Cr_2O_3 was given on the weight of the hide powder i.e., $7\frac{1}{2}\%$. The washed and dried powders were then analysed for their chrome content,² overall basicity,³ acidity, fixed organic matter,⁴ sulphato acidity,⁵ hide substance, total degree of tannage,⁶ etc. according to standard methods.

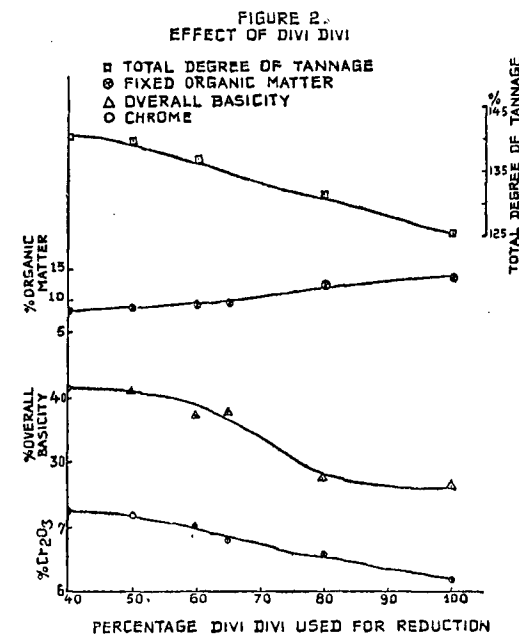
Data and Discussion:

Chrome content: The results are given in Figs. 1 and 2. The decrease in chrome fixation by the hide powder is



due to the increase in the non-ionic and anionic chrome complexes present in the liquors. When non-ionic and anionic complexes are formed, less Cr_2O_3 will be fixed, as should be expected. Gustavson⁷ found that organic chrome com-

plexes fixed decreased chromium, as the amount of organic salts present increased. Procter and Wilson⁸ showed that the tanning action of chrome liquors was checked and some times reversed by the introduction of salts of hydroxy acids.



Basicity: When more divi-divi is used, naturally more quantities of organic degradation products will be produced during reduction and therefore the overall acidity is found to increase i.e., the overall basicity is found to decrease. In the results of the analysis of the liquors also¹ it was noted that the overall basicity of the liquors went on decreasing as more and more of the vegetable tanning material was used in the reduction. Therefore, the present results go to confirm the findings made earlier. The fact that the chrome complex in the leather is having acidity (chrome complex acidity goes on increasing) shows that chrome-vegetable complexes are penetrating and get fixed rather than the basic chrome sulphate and the vegetable tanning matter separately.

That the basicity is only below 40% shows that to make a good leather it is not necessary to have 66 $\frac{2}{3}$ % basic chrome complex which is shown to be 40% basic, actually account for 60% and more if only the sulphato acidity is considered. (See Table I: Official basicity expressed as 100 sulphato acidity). McLaughlin and others did not take into account the acidity due to the organic materials and acids that may be readily displaced by -OH. Because of the increase in Divi-divi used the organic acidity increases, resulting in the decrease of basicity.

Acidity: The sulphato acidity of the chrome complex fixed in the powder is decreasing, when the organic material used for reduction is increased. Previously in the liquor analysis also, it was found that the SO₄ in the complex decreased in the liquors. The acidity due to the organic matter of acidic nature in the complex (i.e., acids other than -SO₄) has been found by subtracting the sulphato acidity and protein bound acidity from the overall acidity. This is found to increase. Therefore, this is another proof that more tannin of an acidic nature or organic acids enter into the chromium complex displacing the SO₄ and other groups. The total protein bound acids and also the protein bound SO₄ were determined. The protein bound acid increases considerably and the protein bound SO₄ increases only very slightly. By the difference between the two, the acids other than SO₄ bound to protein was obtained. This figure goes on increasing in the series, showing that more of the organic acids get fixed to the protein, when the organic matter used in the reduction of bichromate is increased.

Fixed Organic Matter: The percentage fixed organic matter is found to increase with the increase in Divi-divi used for reduction. This may be due to the organic tanning material present within the chrome complex or the free organic matter fixed to the protein or due to both. Whichever of the above is combined, it proves more organic matter

TABLE I

Divi-divi used for 100 gm. bi- chromate.	Cr ₂ O ₃ fixed for 100 gm. of hide substance	Basicity Overall	Official	Fixed Org. matter per 100 gm. hide subs.	Total degree of tannage	Sulphato acidity %	Overall acidity %	M.eq. acid per gram of protein	Protein bound acidity (%)	M.eq. SO ₄ per gm. of protein	Organic acidity of the complex (%)
40	7.246	41.44	74.13	8.812	140.5	25.87	58.56	0.2591	9.046	0.0916	23.64
50	7.181	41.24	75.18	8.950	139.6	24.82	58.76	0.2653	9.346	0.0920	25.59
60	6.997	37.21	76.63	9.137	136.4	23.37	62.79	0.2763	9.991	0.0927	29.43
65	6.814	37.79	78.53	9.600	132.9	21.47	65.21	0.2823	10.48	0.0927	30.26
80	6.565	27.69	80.42	12.09	131.4	19.58	72.31	0.3174	12.24	0.0922	40.49
100	6.165	26.16	82.57	13.12	125.2	17.43	73.84	0.3258	13.37	0.0930	43.04

gets fixed, when increasing amounts of divi-divi are used. With the increase in the amounts of divi-divi used, the liquors behave more closely to the vegetable tanliquors.

Degree of Tannage: The total degree of tannage calculated according to the method suggested by Kubelka goes on decreasing gradually. Total degree of tannage is calculated as Degree of tannage due to chrome Degree of tannage due to vegetable — Cr_2O_3 fixed $\times 2.73 \times 6.66$ degree of tannage due to vegetable. The vegetable tanning matter present and fixed is comparatively very low as seen from the percentage of fixed organic matter. The increase in the fixed organic matter is very meagre when compared to the decrease in the degree of tannage due to chromium alone. Therefore, when the total degree of tannage is calculated, there is a gradual fall. With the decrease in chrome content and with the increase in vegetable matter as indicated earlier, the degree of tannage due to chrome decreases considerably.

With a view to elucidate further the mechanism of tanning of these veg-chrome liquors, experiments were carried out varying the chrome concentration and the effects of pH, salts such as sodium chloride, oxalate were studied. The washed and air dried powders were analysed for their chrome content, fixed organic matter etc. For these experiments, the liquor No. 10 (reduced with 100% divi-divi on dichromate) was chosen, because it contained apart from basic chrome salts, a considerable amount of excess organic material and it would represent a veg-chrome liquor.

When the amount of Cr_2O_3 given is much less than what is required to just tan the powder, almost all the chromium given is taken up by the hide powder. When the amount is increased, only a certain percentage of the given Cr_2O_3 is taken up, until the equilibrium is reached between the liquor and the hide powder. When an increasingly high percentage of Cr_2O_3 is given, only a small

fraction of it is utilised by the hide powder. The general trend of increasing fixation of chrome by the hide powder is due to the concentration effect.

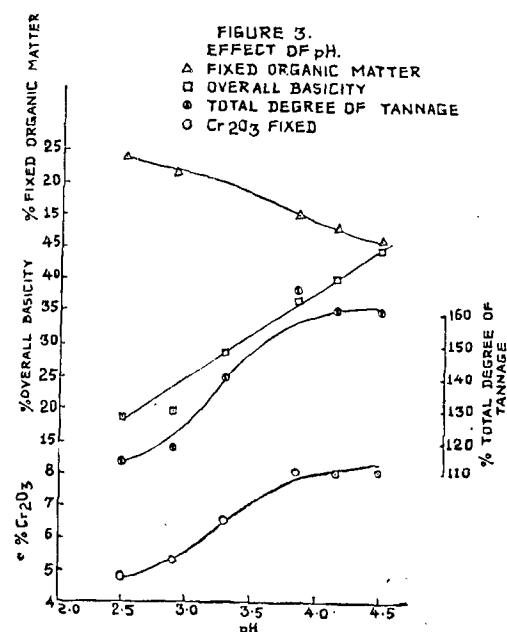
TABLE II
Effect of chrome concentration

Cr_2O_3 given for 100 gm. hide powder.	Cr_2O_3 fixed per 100 gm. hide substance.	pH of tanning equilibrium.	% Cr_2O_3 fixed to Cr_2O_3 given.	Overall basicity.	Fixed Org. matter/100 gm. H.S.
1.5	1.357	4.60	90.46	42.76	4.69
4.5	3.287	4.40	73.05	33.28	11.91
7.5	5.234	4.10	69.77	32.17	12.52
10.5	6.720	3.80	64.00	31.66	14.22
13.5	7.989	3.55	59.19	30.47	15.80
18.0	8.637	3.40	47.97	30.29	17.10

The small decrease in basicity and the variation in pH are due to concentration of Cr_2O_3 in the tanning bath. Considering the percentage of fixed organic matter, it is found to increase when more chrome is given, proving that the organic matter or the vegetable tanning material is associated with chrome. When more liquor is given, more vegetable tanning matter is also available for the powder, along with chromium. It may also be noted that slight decrease in pH with increase in the concentration of chrome assists the fixation of more vegetable tanning organic material.

In the chrome tanning processes, it has long been established that at low pH values, the penetration of chromium is fast, but fixation is low and when the pH is raised, the basicity of the liquor and the tanning property are increased and more chromium is therefore fixed. The

results obtained go to confirm that chrome vegetable complex behaves similar to basic chrome complex. When the



pH is raised, the basicity of the liquor is increased and consequently the overall basicity of the hide powder also increases.

TABLE III
The effect of pH:

pH	Cr ₂ O ₃ fixed per 100 gm. hide substance.	Overall Basicity.	Fixed Org. matter per 100 gm. Hide Subs.	Total degree of tannage.
2.5	4.829	18.58	24.08	111.9
2.9	5.365	19.58	21.80	119.4
3.3	6.598	28.88	20.07	140.0
3.85	8.130	36.59	15.55	163.5
4.15	8.079	40.10	13.22	160.1
4.5	8.153	44.94	11.37	159.7

Considering the fixed organic matter, it is a well known fact that the vegetable tannin fixation is more if the pH is low. The liquor No. 10 contains vegetable matter complexly held in the chrome complex and also excess of free vegetable tanning material. The free vegetable tanning material naturally is fixed at low pH values along with the chrome vegetable complex. Therefore, there is high content of fixed vegetable organic matter. As the pH is raised more of chrome-vegetable complex is fixed, but only less of free vegetable tanning material is fixed.

The total degree of tannage rises when the pH is raised, because of the increased amounts of Cr₂O₃ fixed.

In short, in the pH 2.5-4.5, the liquor shows predominantly the properties of the vegetable tanning material, at low pH values and those of basic chrome liquors at higher pH values. Therefore, by adjusting the pH values during tanning, the characteristics of the final leather can be altered, according to requirements.

TABLE IV

Effect of sodium chloride:

Moles of NaCl per mole of Cr ₂ O ₃ .	pH of tanning equilibrium.	Cr ₂ O ₃ fixed per 100 gm. hide subs.	Overall Basicity.	Fixed org. matter per 100 gm. hide subs.
0	3.95	9.830	27.93	13.20
2	"	7.773	28.23	14.21
3	"	7.204	26.56	12.74
4	"	6.916	27.99	12.45
6	"	6.837	27.14	13.69
8	"	6.720	28.63	13.95
10	"	6.585	27.47	13.31

The difference in chrome fixation is not much because there is already present some neutral salts formed during the course of reduction of bichromate. However, the data

indicate the trend of the effect of neutral inorganic salts added. The decrease in chrome uptake due to neutral salt effect, when tanning with basic chrome liquors was observed earlier.¹⁰⁻¹² This effect was variously attributed to the well known hydration capacity of the salts¹³ to the formation of more complex compounds of lessened reactivity¹⁴ to the fundamental modification of the hydrolysis of the liquor and membrane action,¹¹ and to reduced accessibility of the reactive protein centres caused by the lyophobic character of the salt and to the saturation of minor electrostatic charges responsible for that portion of the chromium fixed by the residual valency forces.¹⁵ Similar effects may occur with chrome-vegetable complex. Tanning with basic chrome liquors, the overall basicity was shown to be the same regardless of the amount of added salt. The results obtained go to prove that chrome vegetable complexes behave similarly.

Regarding the fixation of organic matter, the data show no apparent change in the percentage fixed. In vegetable tanning, it was reported that salts of strong acids had a greater effect on the rate of fixation rather than the amount of tannin fixation.^{16, 17}

TABLE V
Effect of sodium oxalate:

Moles oxalate per mole of Cr_2O_3 .	pH		Cr_2O_3 fixed per 100 gm. hide subs.	Overall Basicity.	Fixed org. matter per 100 gm. H.S.	Total degree of tannage.
	Initial.	Final.				
0.0	4.25	3.10	7.621	27.81	13.80	152.3
0.5	4.35	3.25	7.466	29.41	13.88	149.7
1.0	4.45	3.6	7.308	29.76	13.78	148.7
1.5	4.55	3.95	6.974	32.39	18.70	140.5
2.0	4.60	4.42	6.266	35.50	13.33	127.3
2.5	4.675	4.70	4.867	32.69	13.25	101.7
3.0	4.725	5.15	4.227	34.52	13.18	90.10

When sodium oxalate is added, to a chrome liquor, oxalate will enter the complex, as it has got the highest penetrating power. This entry will alter the nature of the chrome complexes present in the liquor, reducing the capacity of the complexes to combine with collagen. This is the reason why there is a reduced fixation of chrome when oxalate is added. This kind of reduction in fixation had been reported earlier in regard to basic chrome liquors.^{18, 19} But this reduction in chrome fixation with veg.-chrome liquors is not so marked as in the experiments done with sulphur dioxide reduced liquor.²⁰ Tanning with sulphur dioxide reduced liquor to which two moles of sodium oxalate were added to one mole of Cr_2O_3 , there was reduction in chrome fixation from 7.4 to 1.74%. But in the case of veg.-chrome liquors, it may be seen that the reduction is only from 7.5 to 6.3. Therefore, it may be concluded that the effect of addition of oxalate is not as pronounced in the case of veg.-chrome liquor as in the sulphur dioxide reduced liquor. This is probably due to the difference in the complex and also the presence of other acids and salts and degraded products of the vegetable tanning material. The increase in pH value of the chrome liquor when oxalate is added is in accordance with the findings of Kuntzel.²¹ This increase in pH in turn will raise the basicity of the liquor and thereby causing an increase in the overall basicity of the leather tanned with it. This is shown to be the case, but the increase is only very little.

The percentage of fixed organic matter is only very slightly affected. It can be taken that there is no appreciable change. Oxalate has been shown to have no effect on the fixation of vegetable tanning. This applies to the veg.-chrome liquor also.

As the chrome fixation decreased at a rapid rate naturally also should the total degree of tannage decreases.

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A NOTE ON THE CONTROL OF SOME DERMESTID BEETLES BY BIOLOGICAL METHODS

During the recent years the development of very effective chemical insecticides has been of much help in the control, of insect pests. Along with such methods of control, the Biological control of insects have also been adopted in the control of agricultural pests with much success. In this method of control, the insect pests are usually controlled



Picture Showing the Parasitised Beetle Larva

with the help of other insects, which happen to be their natural enemies. Such helpful insects which parasitise on Dermestid larvae which damage hides and skins have also been known to occur.^{1, 2, 3} Recently the authors came across

a Bethylid parasite attacking the larval forms of the beetle *Anthrenus vorax*.

The *modus operandi* of this method of control is briefly described below. The beetle larvae are attacked by the female Bethylid, which goes on stinging and killing them. On some of these larvae the bethylid parasite lays her eggs. Further development of the bethylid larva takes place at the expense of the beetle larva. In the course of development, the bethylid larva sucks up and digests the tissues of beetle larva, ultimately reducing it to an empty skin. Thus quite a large number of beetle larvae are destroyed by the Bethylid parasite. This may probably prove useful in the control of insect damage to hides and skins by beetle larvae. The observations made on this insect will be published in due course.

Bacteriological Laboratory,
30—5—1957.

R. BHASKARAN & S. N. SEN.

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RESEARCH BEARS FRUIT

Practical Demonstration No. 5

Process No. 2

Manufacture of Glace Kid leather by two bath chrome tanning method *

J. C. DEB.

Raw material : Wet salted (Erode) prime quality goat skins of average size 32" to 36" are taken.

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

Liming : (By paste method in flooding system).

Unhairing is done by painting a depilating paste of the following composition :

Sodium sulphide—1 part, i.e., 4 lbs.	} for the pack of 100 skins.
Sodium chloride—5 parts 20 lbs.	
Slaked lime —15 parts 60 lbs.	

Sodium sulphide and sodium chloride are dissolved separately in water. The two solutions are then added to the mixture of lime and water. Care is taken to get a homogeneous paste, cooled to the room temperature. It is better to prepare the paste in two days advance before the application on the skin.

Process demonstrated to the tanners from 5th June to 8th July 1957.

The paste is applied to the flesh side of the skin. The skins are then piled up in a pit flesh to flesh. The pile is flooded with water and kept undisturbed for 5 days. On the sixth day, the skins are taken out, unhaired and put into new lime liquor containing 5% lime on the soaked weight of the skin, in a paddle for one day. Next day the skins are examined to get sufficient plumpness and taken out, fleshed, scudded, weighed and washed thoroughly in running water at 86° to 90°F for 20 minutes in a paddle and ready for bating.

Bating: (Overnight bating method is followed).

The washed skins are bated in a covered paddle using 1 to 1.5 per cent Pancreol 5A on the fleshed weight. The bath is made with half the quantity of bate using one paddle of water (300% at 95°F and the skins are run for one hour). After running one hour 2 ozs. of potassium or sodium flouride, per 100 gallon of water dissolved in one pint of water at 105°F is added to the bath and the bath is run for 5 minutes. The skins are left in the bath overnight, keeping down the temperature of the bath at 90°F.

Next morning the remaining half of the bate is added and the temperature of the bath is raised to 100.4°F by passing steam. The skins are paddled in the bath controlling the temperature of the bath at 100.4°F until satisfactorily bated. The pH of the bate liquor before unloading should be 7.8 to 8.0, if not it should be adjusted to that of pH.

The exact stage when the bating can be regarded to have been satisfactorily completed, is generally judged by the following indications:—

(1) The skins should be thoroughly delimed and phenolphthalein applied to the edge of a cut piece of bated pelt should not show a red colouration.

(2) The bated skins should be absolutely fallen and flaccid and should lie in any position in which it is kept. They should not show any tendency to spring back. The absence of the tendency to spring back is generally tested by pressing the grain of the skin by the thumb and the thumb impression should remain.

(3) When bated skins are scratched on the grain by the thumb nail the scud consisting broken hair roots, other epidermal remnants, dirt, etc., should easily come out showing that the scud has been thoroughly loosened and rendered easily removable.

(4) When air is enclosed by folding the bated skin in the form of a pouch and the pouch is squeezed by the hand and made smaller and smaller in volume, then all the enclosed air should come out producing air bubbles on the surface of the pouch. This shows that the pores of the skin have been thoroughly opened out.

(5) When the flesh side is scratched by the thumb nail the adhering flesh should be removable when some pressure is applied, but the flesh should not be too easily removable, as in the case of overbating.

After the completion of bating the skins are taken out, sendded well, washed in cold water of 86° to 90°F, weighed and then immediately put to the tanning process.

Tanning:—Tanning is done by the double bath process in a drum as described below:—

Chroming bath	% on the bated pelt wt.
Bichromate of soda	.. 5-6
Hydrochloride acid	.. 2½-3
Water	.. 200-250

The skins are put into the bath, worked for 4 hours and then kept overnight. Next morning the skins are worked for some time in the bath. They are then taken out and

piled up on a platform to drain, covering with a gunny and left for overnight.

Next morning the skins are struck out well by a striking out machine or a hand slicker. They are then put to the reducing bath as described below.

Reducing bath.	% on the bated pelt wt.
Anhydrous sodium bisulphite ..	8-10
Water ..	250-300

Bisulphite is added in 8 equal instalments at an interval of 30 minutes.

The bath is made in a drum or covered paddle with $\frac{1}{4}$ of the above bisulphite, the skins are quickly put into it, run for half an hour followed by the addition of the second instalment of bisulphite. Bisulphite is added at half an hour intervals with continuous working of the skin until the eighth instalment of the bisulphite is added. The working of the skin is continued for 8 hours in all, and the skins are kept overnight in the reduction bath. Next morning run the drum for one hour. Check the pH. The pH of the skin should be 3.3 to 3.5. The skins are then washed in diluting the reduction bath for 10 to 15 minutes and piled up on the platform for three days to drain off the excess of moisture.

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

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

	% on the shaved wt.
Sodium bicarbonate ..	$\frac{1}{2}$
Water ..	200

The bath is made in a drum at room temperature. The skins are put into it, worked continuously for half an hour and then tested for proper neutralisation with bromo-cresol-purple as indicated by the purple colour on the leather surface and yellow colour in the middle layer of the leather. The skins are then taken out and washed twice with plain water. They are then ready for dyeing and fatliquoring.

Dyeing and fatliquoring: For blacks the skins are dyed with the following compositions:—

	% on the shaved wt.
Chlorozal black ..	1
Nigrosine ..	$\frac{1}{2}$
Methic leather black D ..	$\frac{1}{2}$
Formic acid ..	$\frac{1}{2}$
Water ..	200 at 130°F.

Before putting in the dye bath the skins are first drummed in water at 104°F to attain that temperature for 10 minutes. The conditioned skins are then put, turned over (grain side out) into the drum containing 200% water at 130°F. chlorozal black dissolved in water is added in the drum. Start the drum and run for 15 minutes. Then add nigrosine, dissolved separately and run the skins for 15 minutes or more. The Methic leather black D is also dissolved separately and added to the drum and run for further 15 minutes. Lastly added the formic acid and run the drum for 10 minutes more.

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

	% on the shaved wt.
Neat's foot oil ..	$1\frac{1}{4}$
Egg oil (or egg yolk) ..	$\frac{1}{2}$
Cremol F ..	$\frac{1}{2}$
Castor oil soap solution (10% solution) ..	$\frac{1}{4}$

pH of the emulsion of the fatliquor is adjusted to 7.8-8. Then 2% Quebracho extract dissolved separately is added to the exhaust fatliquor bath and run for 30 minutes. The skins are then taken out and horsed up overnight.

Striking out and oiling up :

Next day the skins are struck out on the flesh and grain side. Neat's foot oil is applied on the grain side and hung up in the shed for sammying.

Sammying setting and drying :

After oiling up, the skins are sammed, set out and dried in the shed.

Finishing :

(a) *Sawdusting, staking and buffing :* The dried skins are stored for some days for conditioning. They are then saw-dusted overnight in moist saw-dust to condition them for staking. The conditioned skins are staked first slightly by a Slocomb staking machine. Then they are piled up on the floor in several packs containing one dozen skins in a pack for overnight. Next morning the skins are staked again by the same machine with considerable pressure. They are then aired off a little and buffed on the flesh side by the buffing machine using 120 grit emery paper.

(b) *Trimming and ironing :* Next morning the buffed skins are trimmed and ironed on the grain side by a hand electric iron. The skins are now ready for seasoning.

(c) *Clearing, Seasoning and glazing :* The skins are first cleared with 10% ammonia solution on the grain side, dried and then given two successive bottom season coats on the grain with the following bottom season.

Nigrosine	..	1 oz.
Lissamin green	..	7 gms.

CLRI black pigment	..	6 ozs.
„ M. G. binder	..	4 ozs.
„ Glazing finish	..	8 ozs.
Ox blood	..	20 ozs.
Milk	..	16 ozs.
Isopropenol alcohol	..	2 ozs.
Diethylene glycol	..	1/2 oz.
T. R. O.	..	1/2 oz.
Ammonia	..	1 oz.

Water to make one gallon.

After application of two successive pad coats with the above, the skins are dried, glazed and then given a top season coat.

Top season

Bottom season	..	2 1/2 lbs.
C.L.R.I. M.G. binder	..	4 oz.
„ glazing finish	..	8 oz.
Milk	..	12 oz.
Blood	..	8 oz.
Formaldehyde	..	6 oz.

Water to make one gallon.

One coat of the top season is applied to the grain side with pad, dried and then apply the fixing coat by spraying with

10% casein solution	..	1 part
Formaldehyde (40% strength)	..	1 part
Water	..	6 parts

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

Final glazing:

Inclined bed glazing machine is the best. First glazing is done under heavy pressure moving the skin all round.

The glazing produces glass marks on the grain which are smoothened out by glazing under light pressure, the second time. The glazing is skillfully done without producing pleats.

Measuring, smooth plating ironing, grading and packing:

The glazed skins are then measured and then smooth plated by hydraulic press at 150°F with light pressure. The skins are then ironed with an electric iron if necessary and then sorted, graded according to substance into 3 or 4 classes they are then packed with 24 skins in a bundle.

TECHNICAL SEMINAR

Photometric Titration Technique *

D. RAMASWAMY

Photometric titration technique of determining the titration equivalence points quantitatively is an elegant and recent innovation. The fundamental law applied is the usual Lambert-Beer Law and the principle implies the measurement of monochromatic light absorption at different amounts of addition of titrant. Since the absorbance is directly proportional to concentration, the plot of absorbance vs. titrant added will consist of two straight lines intersecting at the end point and the shape of the curve will be dependant on the absorbing properties of the reactant, titrant and the products of reaction. The main advantages with the photometric titration device over colorimetry and potentiometry are (i) the non-interference due to other absorbing substances present, (ii) in systems where reactions tend to be incomplete at the equivalence point since end-points are easily determined by extrapolation, (iii) in turbidimetric determinations where absorption characteristics are not reproducible and (iv) the very low concentrations that are employed. The factors that affect the accuracy of titration due to (a) dilution errors, (b) cell characteristics, (c) temperature changes, (d) solvent absorbance, (e) selection of wave-length and (f) choice of scale in plotting and (g) stray light errors may be eliminated or atleast reduced to the minimum if necessary precautions are taken during the titration and if the assembly is designed properly.

The applications and developments of the technique in various branches of analytical chemistry, viz. precipitation

* Summary of the paper read at Seminar held on 3rd May, 1957.

reactions, oxidation-reduction systems, complexation reaction and neutralisation reactions have been phenomenal. There are definite advantages by making use of this technique in neutralisation reactions, particularly those of weak acids and their mixtures. The technique is capable of giving accurate end points for weak acids between pK_a values of 10^{-3} to 10^{-8} . Several useful determinations like mixtures of nitrophenols and acetic acid etc. have been carried out photometrically. The technique is also useful in fundamental studies for calculation of dissociation constants, finding out strengths of acids etc.

The potential uses of the technique in leather field are ample. Two of the problems receiving attention at this Leather Institute are (i) the differential titration of phenolic groups of the vegetable tanning materials and (ii) the total weak acids present in the tanliquor. Data have already been obtained and published on both these phases. The possible applications of the technique are manifold and full exploitation of the technique may reveal interesting results.

ECAFE Working Party for Leather, Leather Goods and Handicraft Meeting

Y. NAYUDAMMA

Recognising the importance of the leather industry in the ECAFE region, the Fifth meeting of the ECAFE Working Party on leathers, leather goods and handicrafts marketing was held at the Central Leather Research Institute between the 17th and 24th June, 1957. Sri C. V. Narasimhan, Executive Secretary of the ECAFE in his address pointed out the main problems facing the leather industry in the ECAFE region and the scope for improving this industry by proper animal husbandry and prevention of wastage.

Professor Thacker, Director-General, Scientific and Industrial Research, in welcoming the delegates of the ECAFE Working Party to the Central Leather Research Institute had very generously offered to throw open the facilities available at the Central Leather Research Institute for research, training of personnel and technical know-how to the good neighbours of India in the ECAFE region.

Shri R. Venkataraman, Minister for Industries, Government of Madras, inaugurating the Conference on the 17th June, recalled India's efforts to expand the activities of the ECAFE and indicated the many ways by which Government is anxious to promote the growth of this very valuable industry in India and particularly in the South. An Institute for Footwear Technology is soon to be opened in Madras to train 100 persons to become operators, foremen and

works managers. He suggested that the Working Party might examine all aspects of the leather industry and offer useful suggestions which could be implemented immediately by the Governments concerned.

Over 35 delegates from different countries such as Burma, France, Afghanistan, Japan, Netherlands, Pakistan, U.S.S.R. Indonesia, U.S.A., Federation of Malaya, Yugoslavia etc., attended this Working Party Meeting, and Sri Satish Chandra, Leader of the Indian Delegation was elected Chairman for this Meeting. The Working Party held six technical sessions in which various problems of the leather industry in this region have been discussed in detail. The reports from the different countries on the development of small-scale industries in general and of leather industry in particular, were considered and the countries have agreed to exchange useful information in regard to the materials, methods and means to be used for the development of the small-scale industries.

In regard to the promotion and coordination of research in the leather industry of this region, it was noted with satisfaction that good work is being done in India, Indonesia and Japan. Members were of the general opinion that the Central Leather Research Institute offers extraordinary facilities for research and the countries in this region could take the best advantage of this Institute. The generous offer made by the Director-General, Scientific and Industrial Research, to throw open the technical know-how and the facilities for research and training available at this Institute to the countries in this region has been gratefully acknowledged and the exchange of research programme, publications and personnel has been suggested. Active co-operation, co-ordination and collation of the work conducted in the Institutes of Indonesia, Japan and the Central Leather Research Institute were recommended.

One of the sessions was devoted to the discussion on the economic aspects of tanning and the productivity in leather industry in this region. The papers presented by the ECAFE Secretariat offered a wealth of information in regard to the economic aspects and productivity. Though Asian countries were remarkably well-endowed with livestock having more than 270 million heads, the need is felt for taking immediate measures for improving the quality of livestock, for better animal husbandry and better economic returns for the live and dead animal; for using better methods of flaying and preserving, collection, grading and movement of raw hides and skins in this region. The necessity for devising standards for leathers to be exported in the region was discussed. It has been suggested that each country may establish some kind of standards which could be further collated to work regional standards at a later date. The needs, problems, trends and personnel in the field of small scale industries and the technical assistance to be offered by the U.N. and their agencies were also considered.

In the concluding session, the programme of work and the priorities, the date and place of the next meeting were considered and this was left to the ECAFE Secretariat to finalise the programme in consultation with the participating countries.

Market Clinic: One of the activities of this Working Party is the Market Clinic. The experts from the various countries went round the exhibition, assessed the finished leathers and leather goods and suggested methods and means to improve the tanning, finishing and marketing of these goods. The clinic also served to cure the ills of the industry. Many trade enquiries brought from the tanners were attended to by these leather experts and suitable remedies suggested.

Exhibition: Concurrently with the Working Party meeting, an exhibition was arranged at the Central Leather Research Institute. Exhibits from various countries like Indonesia, Japan and Burma and from various parts of India were displayed.

Finished leathers, leather products and leather auxiliaries were exhibited. Over 500 people visited the Exhibition. Mr. C. Subramaniam, Minister for Finance and Education, Madras State, in opening the Exhibition assured the Working Party that the Government is fully aware of the good work done by the ECAFE and that the Government assured possible help to the Industry. The Exhibition has afforded a good opportunity to compare notes in regard to the quality of leathers and leather goods that are prepared in this region and to improve on their quality. It also provided an opportunity to the members coming from different countries to satisfy themselves with the quality of leathers and leather products made in India, which may further improve the Indian export trade.

"Open Forum": The Central Leather Research Institute arranged for an "Open Forum" so that the Indian tanners and the foreign experts may meet face to face and discuss their problems. The subjects discussed in this forum were: (a) "Raw hides and skins and their improvement" and (b) Marketing of hides and skins, leathers and leather goods in the ECAFE region. This "Open Forum" was well attended and was presided over by Mr. R. K. Rangan, Chief Controller of Imports and Exports. This provided an opportunity for the local tanners to get first-hand information about prospects for improving their trade.

"Open House": The Central Leather Research Institute had an "Open House" concurrently with the Working Party meeting. The public was welcome to go round the

Institute and see for themselves the activities of the Institute. Over 500 people went round the Institute during this period.

Visits to factories: The members attending the Working Party meeting from the various countries visited two well organised commercial tanneries and three East Indian tanneries that worked on cottage basis, the Government Footwear Production centre, the slaughter house etc. and the Central Leather Research Institute to acquaint themselves with the progress of the Indian leather industry.

"At Home": The Central Leather Research Institute was "At Home" to the delegates of the ECAFE meeting on the 21st June, 1957. Dr. A. Lakshmanaswamy Mudaliar, presiding over the function, recalled the co-operation and good-will extended to this Institute in a great measure by people in the leather industry and the many-sided activities of the Central Leather Research Institute and of the Government to develop the industry. He thanked the ECAFE for having organised their meeting here and for the active work and valuable suggestions given at the meeting. As Vice-Chancellor of the Madras University, he promised to offer the necessary facilities for students coming from countries of this region for their training towards B.Sc. (Tech.) Degree in Leather Technology of the Madras University.

Mr. Jamal Mohideen and Mr. Anwar representing the Indian tanning industry paid tributes to the Central Leather Research Institute and the services rendered by this Institute to the Indian industry and welcomed the Working Party members to Madras. On behalf of the delegation, Miss S. Partroesti of Indonesia, Mr. Khurshid Ahmed Siddique of Pakistan and Mr. Julius C. Schnitzer of United States of America were all praise for the Institute and for the good work that is being done. They thanked the authorities of the Central Leather Research Institute as well as the

Governments of Madras and India for the excellent arrangements made for the successful completion of this meeting.

The Central Government, the ECAFE Secretariat, the Government of Madras, the Leather Export Promotion Council, and the Governor of Madras were also at home to the delegates during this period.

CLASSIFIED ABSTRACTS

PROCESS PRIOR TO TANNING

INORGANIC CHEMISTRY OF CHEMICALS USED IN LIMING. R. Appel, *Das Leder*, 8, 1, 1, (1957). The aqueous solutions of the chemicals, used in liming, like $\text{Ca}(\text{OH})_2$, NaHS and NaCl with respect to the hydrogen ion concentration and the solubility changes of $\text{Ca}(\text{OH})_2$ through the addition of salt are discussed. In addition a graphical method is described which makes it possible to determine quickly the concentration of the ions and also pH-values in the H_2S -system.

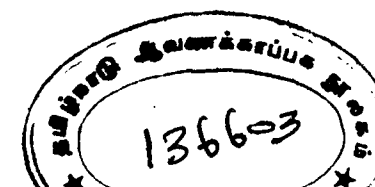
DEGREASING IN THE LEATHER INDUSTRY. G. W. Douglas, *Tanner*, 2, 12, 11, (1957). The excessive grease that is present in raw hides and skins, if not removed, gives rise to 'greasy bands' and discoloured patches on the leather and the leather will be empty and loose due to loss of fibre substance. The removal of grease which causes various faults in the finished leather from hides and skins prior to the tanning operation is of considerable importance to the tanner. The various methods for removal of grease and the economics of these methods are discussed. The paraffin degreasing process using kerosene is found to be a cheap and reliable process for grease removal for an average tanner provided the process is controlled.

K.S.R.

CHROME TANNING

STUDY OF CHROMIUM III SULPHATE COMPLEXES BY ELECTROPHORESIS ON FILTER PAPER. S. Kertes and M. Lederer. *Anal. Chim. Acta.*, 16, p. 40, (1957). The radio activity ratio between the sulphate band and that of the various coloured $\text{Cr}(\text{III})$ complexes was measured and a quantitative estimate of the amount of sulphate complexed under various conditions obtained.

Paper electrophoresis in combination with radioactive tracer techniques thus permits the investigation of the reactions of



Cr^{+3} with SO_4^{-2} . In cold solutions sulphate anions are taken only slowly but at elevated temperature there will be rapid uptake. The results also show that green solutions contain invariably complexed sulphate ionic groups.

Y. N.

OTHER TANNAGES

NEW APPROACHES TO WHITE LEATHER. Ian C. Somerville. *The Lea. Manfr.* No. 3, 12, (1957). Brief historical development of various tanning processes using formaldehyde, alum, chrome, syntans, zirconium and resins to produce white leather were reviewed and some recent developments in each of these types alone and in combination were outlined.

K. S. R.

THEORIES

NEW ELECTRON MICROSCOPIC RESEARCHES ON COLLAGEN, K. Kuhn. 8, 2, 25, (1957). New aspects of electron microscopic researches on fully grown collagen and reticulin fibrils as also the precipitation products of dissolved collagen are reported. Further electron microscope pictures of collagen fibrils, in which silver particles are periodically deposited through oxidation with periodate are also given.

THE COMPARATIVE SUSCEPTIBILITY TO COLLAGENASE AND TRYPSIN OF COLLAGEN, SOLUBLE COLLAGENS AND RENAL BASEMENT MEMBRANE. Ellis Dresner and Maxwell Schubert. *J. Histochem, Cytochem.*, 3, 360-8, 1955. *Via Brit. Gel. & Glue Res. Assoc.*, 8, 1, 23, (1957). A comparative study has been made of the susceptibility to trypsin and to collagenase of collagen and some proteins thought to be related to it. These include a crude reticulin made from embryonic calf renal mid-cortex and soluble collagens initially extracted from skins at alkaline or acid reactions. With minor variations all these materials are readily hydrolysed by collagenase and are rather resistant to trypsin. In all cases of hydrolysis by collagenase the solubilized portion contains hydroxyproline only in peptide form.

NOTE ON THE INFLUENCE OF NITROUS ACID ON COLLAGEN Das Leder, A. Kuntzel, 8, 2, 34, (1957). The nitrous

acid, formed by the action of acetic acid or sulphuric acid on sodium nitrate acts differently on many amino acids of collagen, without effecting its structural nature. Mostly effected amino acids are lysine (deamination), arginine (transformation of the guanidyl group into a cyanamide group), and tyrosine (introduction of nitroso nitro and diazo groups). To a lesser extent serine and threonine are effected. Contrary to the statements in literature, the nitrous acid is allowed to form inside the fibres the collagen structure is loosened.

EFFECTS OF DIFFERENT CHEMICAL AND PHYSICAL FACTORS ON A SOLUTION OF COLLAGEN A. A. Delaunay, S. Bazin and M. Henon—*Compt. Rend.*, 1955, 241, 907-9. *Via. Chem. Abst.*, 1956, 50, 7192f. *Thro' Brit. Gel. & Glue Res. Assoc.* 8, 1, 18, (1957). Collagen A was prepared as described by the authors (*C.A.*, 50, 3511f). Adjustment of pH from the normal value of 4.3-4.5 to pH 2.5 and 3.5 with HCl prevents formation of a collagen precipitate upon adjustment of the solution to 0.472M Sodium chloride. Adjustment with 0.1N sodium hydroxide to pH 4.9 yields a very viscous solution which congeals when the pH is raised to 5.55-7.0. Heating removes or diminishes the capacity of collagen solution to be precipitated by sodium chloride. A solution of collagen A heated to 40° for 3 minutes (crit. temperature) and cooled abruptly thereafter will not yield a precipitate in the presence of 0.422M sodium chloride. However, a precipitate is formed with this salt concentration if the cooling is slow, or if the salt concentration is increased to 0.85-1.7M. Highly acid solutions (pH 2-3.6) when heated at 40° for 3 minutes behave as do solutions of pH 4.3-4.5. Solutions of pH 7.5 heated similarly become viscous and spontaneously form fibrils. The saline-collagen precipitate is not dissolved by heating 3 minutes at 40°, but is rapidly and completely dissolved at 48° and higher, though a slight turbidity may reappear after 24 hours. 0.5M sodium cyanide does not precipitate collagen A, and also prevents the precipitation normally produced by sodium chloride, sodium bromide, sodium iodide and sodium salicylate; similarly, 0.085M sodium tartrate does not precipitate collagen A, and inhibits precipitation produced by sodium chloride, sodium sulphate, and sodium salicylate. 0.085M calcium chloride and 0.213M lithium bromide lower the critical temperature. Formaldehyde at pH 4.3 produces a thixotropic gel in approximately 1 hour; the formol-collagen precipitates, but less readily,

in the presence of salts. Combinations of xylose, glucose, fructose, galactose, maltose, and sucrose with various concentrations of sodium chloride, sodium bromide, sodium iodide, sodium sulphate and sodium salicylate gave results ranging from no precipitate to normal precipitation.

THE ROLE OF NONPROTEIN CONSTITUENTS IN THE FORMATION OF THE PROCOLLAGEN STRUCTURE. A. L. Zaides, A. A. Tustanovskii, and G. V. Orlovskaya. *Doklady Akad. Nauk, SSSR*, 104, 563-6, 1955. Via. *Chem. Abst.*, 50, 9826b., (1956). Thro' *Brit. Gel. & Glue Res. Assoc.*, 8, 1, 20, (1957). The effects of lipides and polysaccharides on the striated structure of collagen were studied. Electron-microscope and X-ray methods under small incidence angles showed that the observed striation is not caused by an inter-weaving or other arrangement of polypeptide chains, but by specific interaction of protein with polysaccharides. The relatively easy separation of most of the polysaccharides from the protein shows that they combine by bonds weaker than covalent, possibly by hydrogen or electrochemical bonds. Lipides do not cause formation of the electron-microscope procollagen structure. X-rays under large incidence angles do not reveal the complexes formed by combination of procollagen with polysaccharide, but only the actual protein structure.

LOW ANGLE X-RAY DIFFRACTION PATTERNS OF COLLAGEN. S. G. Tomlin and C. R. Worthington. *Proc. Roy. Soc.* 1956, 235A, 189-201. Via. *Chem. Abst.*, 50, 14308e, (1956). Thro' *Brit. Gel. & Glue Res. Assoc.*, 8, 1, 19, (1957). Measurements were made of the intensities of upto 25 orders of the low-angle X-ray diffraction patterns of wet and dry collagen fibres from 3 different sources. Patterson functions were plotted. Satisfactory interpretations of the diffraction patterns of wet and dry fibres have been reached. The conspicuous periodic raised bands seen in electron micrographs of metal-shadowed fibres change in length on wetting the fibres, while the regions between them are but little affected, and it is concluded that these bands are highly disordered regions in dry fibres, becoming more orderly on hydration, while the interbands are always well ordered. Some evidence has also been obtained for the existence of an axial periodicity of about 32.8A. A rational treatment of the low-angle X-ray diffraction data of collagen may be based upon the assumption that these diffraction patterns are due to the coarser features of the structure

which are centrosymmetrical, so that the repeat unit is essentially a band and interband structure. From this treatment dimensions of bands and interbands and their variation between the wet and dry states have been obtained. The observed increase in the axial period from 635 to 670A. on wetting dry fibres was found to be accompanied by a relatively large increase in the band length and a slight decrease in interband length. The repeat unit of collagen probably contains 21 or perhaps 22 units of about 32.8A.

TESTING

DIRECT SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM WITH SPADNS. G. Banerjee. *Anal. Chim. Acta*, 16, p. 62, (1957). Thorium complexing agent 2-p-sulphophenylazo-1, 8-dihydroxynaphthalene-3, 6-disulphonic acid (spadns), has been successfully utilised for direct spectrophotometric determination of microgram amounts of zirconium, based on the fact that zirconium forms a crimson-pink soluble complex with Spadns which is stable in acid medium. The stoichiometric composition of the coloured complexes has been determined spectrophotometrically by adopting the "slope ratio method".

Y. N.

INFRARED ABSORPTION SPECTRA OF INORGANIC CO-ORDINATION COMPLEXES. X. STUDIES OF SOME METAL-UREA COMPLEXES. R. B. Penland, S. Mizushima, Columa Curran and J. V. Quagliano. *J. A. C. S.* 79, 1575. Infrared absorption bands of some metal urea complexes have been measured in the 2-35 u region to determine whether co-ordination of urea to a central metal ion involves hydrogen or oxygen as the donor atoms. From a comparison with the results of the calculation of the normal fibres of urea, the absorption bands observed in the metal urea complexes have been assigned. The spectra reveal that urea forms nitrogen to metal bonds with Pt(II) and Pd(II) and Oxygen to metal bonds with Cr(III), Fe(III), Zn(II) and Cu(II).

Y. N.

A MODIFIED NINHYDRIN COLORIMETRIC ANALYSIS FOR AMINO ACIDS. Hyman Rosen, *Archives of Biochemistry and Biophysics* 67, 10, (1957). The method of Yemm and Cocking

was modified to avoid the necessity for the preparation of solutions of reduced Ninhydrin which is an unstable reagent difficult to prepare and to store. The method is as follows:—

To a 1-ml. sample containing 0.01-0.40 μ -mole of an amino acid, add $\frac{1}{2}$ ml. cyanide-acetate buffer and $\frac{1}{2}$ ml. 3 per cent ninhydrin solution in Methyl Cellosolve. Heat 15 min. in a 100° water bath. Maximal color is developed after 10-12 min. Immediately after removing from the water bath, add rapidly 5 ml. of isopropyl alcohol-water diluent. Shake vigorously. Allow to cool to room temperature, and read in a colorimeter at 570 m μ (proline and hydroxyproline at 440 m μ). If the color density in a given series of tubes is too high to determine accurately, further 5-ml. portions of diluent may be added, until the optical densities are below 0.8.

Y. N.

AUTOMATIC DERIVATIVE SPECTROPHOTOMETRIC AND POTENTIOMETRIC TITRATIONS. *Howard V. Malmstadt. LSU Symposium on Anal. Chem., Anal. Chem., 29, 2, 313, (1957).* This presentation shows how some or all of the manipulations inherent in the titration procedure can be removed from the hands of the chemist and automatically performed. An ideal instrument for rapid titrations might be considered one in which the chemist places his sample, presses a button, and a short time later reads the answer from a report sheet. Although such an apparatus is possible for some specific titrations, no one apparatus is, at present, generally applicable to all titrations, and the chemist must decide what instruments and techniques are best suited for his specific requirements. A general discussion of the features and characteristics of existing automatic titration systems is aimed at providing a basis for comparison.

A detailed discussion is presented of the derivative system which requires a minimum of pretitration considerations and is ideally suited as an automatic control device for most of the usual titrations. A discussion of the instrumentation for an automatic derivative control unit points out important design considerations and possible modifications for special problems. The general requirements are presented for utilizing automatic derivative control with potentiometric and spectrophotometric end point detection, and some specific techniques and applications are described.

USE OF A WAX-IMPREGNATED GRAPHITE ELECTRODE IN POLAROGRAPHY. *V. Frances Gaylor, Anne L. Conard and Jean H. Landerl. Anal. Chem., 29, 2, 224, (1957).* Wax impregnation of a graphite rod yields a solid electrode which is superior in several respects for polarographic measurement. Absorption of wax into the electrode pores greatly reduces the high residual currents normally found with the plain graphite rod. Sensitivity to small concentrations of polarographically active species is thus increased by a factor of 10 or more and the reproducibility of both current and potential measurements is improved. The wax-impregnated electrode is applicable to both oxidation and reduction reactions. Satisfactory polarographic data have been obtained on oxidation waves of typical organic compounds of the phenolic, amino, and diamine types, and on reduction waves of typical inorganic species. Half-wave potentials can be measured with a standard error of less than 0.01 volt. Diffusion currents are proportional to concentration and may be used as a basis for quantitative analysis; the standard deviation of current measurements is 2%. Concentrations of 10^{-5} M or lower can be satisfactorily measured in a stirred test solution.

NON-AQUEOUS POLAROGRAPHY. *Paul Arthur, LSU Symp. on Anal. Chem., Via. Anal. Chem., 29, 2, 312, (1957).* Polarography in non-aqueous solvents introduces many new problems, among the most important of which is the curve distortion caused by iR drop in the cell. Commercially available automatic polarographs are designed to plot current as a function of applied voltage and therefore do not correct for iR drop.

A number of methods have been employed to overcome this difficulty—e.g., the use of polar solvents or mixed polar and non-polar solvents to keep the resistance low, the use of low concentrations, so the currents (and thus, iR drop) will be low, and hand plotting of values mathematically corrected for iR drop. Many investigators have employed polar organic solvents and a wide variety of such solvents have been shown to be useful even with conventional polarographs.

More recently, Elving, Arthur, and associates, working independently and using different approaches to the problem, have devised polarographs capable of giving good polarograms even when high resistances are encountered. Elving employs an auto-

matic iR-drop compensator for use with a conventional polarograph, while Arthur employs a function plotter which plots current as a function of effective voltage, the latter being obtained by a high impedance measurement of the potential of the micro-electrode vs. an extra calomel-type reference electrode.

Certain principles must be understood if either Elving's or Arthur's apparatus is to be used effectively.

TITRATIONS IN NONAQUEOUS SYSTEMS. John A. Riddick. *LSU Symp. on Anal. Chem., Via. Anal. Chem.*, 29, 2, 313, (1957). The utilization of acid-based titrations in non-aqueous solvents requires a more extensive knowledge of the nature of acids and bases and factors affecting their strength than when the titrations were confined to water. A resume of the history of the concepts and theories of acids and bases introduces the two most prevalent, those of Bronsted and of Lewis. The six major factors that determine the acidic or basic nature of a substance the structure, resonance effect, electrostatic effect, hydrogen bonding, steric effects, and solvent effects are presented individually. The research analytical chemist has a wide choice of solvents as reaction media. The choice of a solvent depends on the nature of the material to be analyzed—i.e., whether it is acidic or basic and to what extent—whether or not a differentiating or leveling solvent is required, and what means are available for determining the end point. The relationship between strengths of acids and bases in the several types of solvents and methods of expression of strengths is one important question for which no satisfactory answer is available at the present time.

A brief summary of the known applications and limitations precedes a discussion of some recent analytical developments. One of the most interesting developments, mainly by Scandinavian chemists, is the use of titrable derivatives for identification of class types and equivalent weight such as the xanthates of primary and secondary alcohols.

Steric and electrostatic effects are illustrated by the dicarboxypyridines and 2-amino-4-azapentanes and homologs. The effect of the solvent is illustrated by the great difference of the basicity of substituted oxazolines, imidazolines, and hexahydropyrimidines in water and acetic acid, and by the acidity of alkylnitronic acids in water and in mixed solvents.

The work of Brackmann and Meyer on acid functional groups in a microbiologically produced antibiotic-type material introduces the use of non-aqueous titrimetric methods as an aid in the proof of structure.

GENERAL

PRODUCTION OF WATER-SOLUBLE LEATHER GREARING MATERIAL THROUGH OXIDATION OF UNSATURATED OIL WITH BISULPHITE. 1. The sulphiting of Cod oil. A. Kuntzel and L. K. Schworzer, *Das Leder* 8, 1, 5, (1957). The process of making unsaturated oils water-soluble by treating with bisulphite while passing atmospheric oxygen through them, which is till now known only in patents is worked out, taking cod liver oil as an example, for the sulphitation. The most suitable working conditions, namely temperature, time of treatment, amount of oxygen passed through, acceleration by using catalysts and addition of emulsifiers are determined.

PATENTS

FATLIQUORING. BP 762,997. *Via. J.S.D.C.*, 73, 2, 78, (1957). A dry-cleanable leather which if dyed does not bleed into water or solvent is obtained by using as the fatliquor on leather of pH ≥ 5 an aqueous solution of a water-soluble Werner-type complex in which trivalent nuclear Cr atoms are condensated with carboxylic acido groups of $> 9C$, e.g. stearatochromic chloride.

NOTES & NEWS

STANDARD FOR RUSSET LEATHER

The Indian Standards Institution has published an Indian standard specification for russet leather. It is a type of leather which is used in the manufacture of footwear uppers. With the increase in the production of footwear in the country and in view of good prospects for export trade, the quality of uppers has to be maintained. With this end in view, the Leather Sectional Committee consisting of experts, manufacturers and big consumers have laid down in the standard the requirements and the methods of test for this class of leather. The requirements have been arrived at from the data collected by the Central Leather Research Institute and Government Harness and Saddlery Factory.

—*J. Ind. & Trade*, 7, 4, 633, (1957).

C. L. R. I. NEWS

Practical Demonstration No. 5 on the manufacture of Glace Kid has been completed successfully on 8th July, 1957.

The following tanners' representatives attended the demonstration on the Manufacture of Glace Kid.

1. Mr. M. A. Jaleel, 45, Eqbal Road, Vaniambadi.
2. Mr. S. Khalid Amin, P.O.T. Shop, Thirunamallia Road, Pallavaram.
3. Mr. B. Lim, 47, South Tangra Road, Calcutta-39.
4. Mr. Hai Kaug Fa, Chingsue Tannery, Calcutta.
5. Mr. Chin Sue Lim, Shi Fong Tannery, Calcutta.
6. Mr. Chen I Yu, Lim Che Tannery, Calcutta-39.
7. Mr. G. M. Malim, Kulai, Johone.
8. Mr. R. S. Md. Abdul Khader, S.A.L. Tannery, Ellore.
9. Mr. M. S. Ramakrishnan, Light Leathers Private Ltd., Chromepet.
10. Mr. R. Kalyanamurthy, Chrome Leather Co. Private Ltd. Chromepet.

11. Mr. E. S. Subramanian, Handymen Industries Private Ltd., Chromepet.
12. Mr. Hajari Charan Das, Bengal Tanning Institute, Calcutta.
13. Mr. Van Ingen, Mysore.
14. Mr. K. M. Varughese, Chrome Leather Co. (P) Ltd., Chromepet.
15. Mr. Yan Chung Wa, Standard Tannery, Calcutta.
16. Mr. A. Mohamed Oomer, Hangal P.O., Dt. Dharwar.
17. Mr. M. Krishnaswamy, Chrome Leather Co. (P) Ltd.
18. Mr. V. S. Vittal Raj, Monywa, Burma.

Extract from some of the observations on the practical demonstration made by the participants:

Rapid tanning of sole leather:

"Much impressed with the process demonstrated for the rapid tannage of sole leather, Central Leather Research Institute is really a boon to the Leather Industry".

Manufacture of picking band leather:

"Process demonstrated is quite satisfactory. This will be profitable to those concerned. The technologists in the Institute have been very enthusiastic and courteous".

Dressing of E.I. Tanned Skin:

"Appreciate the work done by the Central Leather Research Institute on semi-chrome leathers. Because lot of rejections in E. I. Sheep and goats can be converted into saleable suedes and linings. It helps to the E. I. tanners, to do this process with only few machinery. It is really a very good technique. Hope, Central Leather Research Institute would make similar demonstrations on all processes to improve leather trade".

Manufacture of glace kid:

"Practical demonstration of Glazed kid manufacture introduced by Central Leather Research Institute has been excellent and upto-date method. If such leather can be manufactured in India there will be an ample market from here as well as abroad".

This type of demonstrations in glazed kid manufacture under such modified process is of great help to tanners to develop very good leather saleable to India and foreign markets.

"This type of demonstrations will be very helpful to the Indian tanners for the development of Indian glaze kid industry. As regards the finished leather of both the processes are of high standard glaze kid leather and may be easily compared with any other foreign high standard glaze kid leather".

RESEARCH BEARS FRUIT

Practical Demonstration No. 7

Process: Manufacture of E.I. Kips and Skins.

Period: 6th August 1957 to 16th September 1957.

Place: Central Leather Research Institute, Madras-20.

The E. I. tanner over a period of time has developed a tanning technique that is unique and a leather that has won the acclamation of the world. E. I. tanned hides and skins valued at Rs. 250 millions are exported annually from India. There are over 500 tanneries in South India that practice E. I. tanning. This branch of industry has remained for long essentially a decentralised cottage industry providing employment for a large number of people and fetching large revenues to the State.

The Central Leather Research Institute is located in the very heart of the E. I. Tanning Industry. The E. I. Tanning Industry has generously contributed over two lakhs of rupees towards the establishment of this Institute. The Institute has been established with the singular purpose of helping the tanner and to promote the growth of Indian leather industry. Questions are often asked by the E. I. tanners and very rightly so as what this Institute has done for them.

The basic objective of any research is to improve the existing techniques and to develop newer techniques with a view to produce a larger quantity of better quality leather at a minimum time and price. The new policy undertaken by the Central Leather Research Institute in arranging for practical demonstrations every month on the processes developed through research at this Institute has conclusively proven that research bears fruit. Every month a practical demonstration is conducted at this Institute for the tanner to come and assess the process and the

product. Six such demonstrations have already been conducted and the seventh in this series will be demonstrated during the month of August on the manufacture of E.I. kips and skins by newer and rapid techniques and newer tanning materials.

Researches have shown that though the E. I. tanned leather is unique in its quality, the process is based on empirical knowledge and can stand some modifications. The process is unduly long; a good amount of tanning material is wasted and also it is not necessary to stick to the traditional barks like Avaram that are scarce and costly or depend upon the imported Wattle bark. These barks could be safely substituted by other indigenous barks. The processes worked out at this Institute have shown that in the E. I. tanning of Kips and Skins, the time of tanning could be reduced from 35 days to 21 days, and that the E. I. Kips and Skins could be tanned with Karada bark in the place of the imported Wattle bark. The leathers so produced have been exported and met with the approval of the dressers in England.

These processes will now be demonstrated at this Institute between the 8th August and 16th September, 1957. Processes have already been demonstrated on the better utilisation of the E. I. tanned hides and skins converting them into finished leathers like suedes, linings etc. fetching higher price.

This demonstration coming off in August is yet another contribution of the Central Leather Research Institute to the E. I. Tanning Industry. It is upto you now to come and watch the processes from raw to finish, to assess the economics of the process and the quality of the product and to satisfy yourselves that the processes developed through research are beneficial to you.

If you are satisfied with the demonstration, you are welcome to adopt the process in your own tannery. If you have any difficulties in adopting this process, our research staff will come over to your tannery to implement the process to your satisfaction. If, after watching the demonstration, you have any suggestions or comments to make on the process or how best we could serve you, please let us know.

Arrangements have also been made as usual at this Institute for boarding and lodging of the participants at cost. Please let us know early the name of your representative who will participate in this demonstration.

PROGRAMME

E. I. Tanning of kips using substitutes for Wattle bark and extract.

8th August 1957:	Soaking and 1st liming.
17th " "	: Unhairing and 2nd liming.
21st " "	: Fleshing and scudding.
22nd " "	: Fleshing and scudding.
23rd " "	: Deliming, I bark.
31st " "	: II bark.
9th September 1957:	Bleaching, I myrobing.
11th " "	: II Myrobing.
13th " "	: Oiling.
14th " "	: Sammying, Setting, Drying, Trimming.

Rapid tannage of E.I. Skins:

6th August 1957:	Soaking and Painting.
7th " "	: Unhairing and liming.
9th " "	: Scudding and Reliming.
12th " "	: Fleshing.
13th " "	: Fleshing, Scudding, Deliming. Scudding, pretreatment. I bark.
19th " "	: II bark.
24th " "	: Bleaching and myrobing.
26th " "	: Oiling, hooking.
27th " "	: Sammying, Setting, Drying, Staking Buffing and Trimming.

FUTURE PROGRAMME

The eighth in the series of the demonstrations will be on "Manufacture of Basic Aluminium Sulphate".

The ninth in the series of the demonstrations will be on "Applications of Basic Aluminium Sulphate for (i) white tanning and (ii) retanning of E. I. tanned leathers.

Dr. Y. Nayudamma, Assistant Director-in-Charge, Central Leather Research Institute attended the meeting of the selection Committee held at New Delhi on the 25th and 26th June 1957.

Sri P. S. Venkatachalam, Junior Scientific Officer has been awarded the M.Sc. degree by the Madras University for his thesis on "Studies on semi-chrome tanning".

Sri B. C. Basu, Junior Scientific Officer, has been awarded the M.Sc. degree by the Madras University for his thesis on "Study of Indian Vegetable Tanning Materials".

VISITORS

<i>Name of visitor</i>	<i>Date of visit</i>
Mr. U. Win Baw, Vice Consul for Burma in Madras	21-6-1957.
Mr. Abdulla Yussufi, Director, Agricultural and Small Scale Industries Bank, Kabul, delegate from Afghanistan to the ECAFE Conference	"
Mr. Takahisa Izuchi, Mr. Masao Asoka, Mr. Hanso Ono and Mr. Takatoshi Tanaka, delegates from Japan to ECAFE Conference	"
Mr. D. W. R. Loss, Asst. Agricultural Attache Netherlands Embassy, New Delhi	"
Mr. Khurshid Ahmed Siddiqui, Marketing Officer, Co-operative Marketing Department, Govt. of Pakistan, delegate from Pakistan	"
Mr. Victor M. Lessiovski, Delegate of the USSR to the ECAFE Conference	"
Mr. Ribowo, Mr. Zakatia Raib, Mr. Basuki Wibisona and Miss S. Partroesti, Indonesian delegates to the ECAFE Conference	"
Mr. Julius C. Schnitzer and Mr. George R. Jacobs, US delegates to the ECAFE Conference	"
Mr. Ahmed Bin Perang, Delegate from Malaya	"
Mr. Ernest Taussing and Mr. F. H. Hoek, FAO Experts attending the ECAFE Conference	"

<i>Name of visitors</i>	<i>Date of visit</i>
Mr. P. K. Das, ILO representative	21-6-1957.
Mr. K. B. Panikkar, WFTU representative	"
Mr. C. V. Narasimhan, Executive Secretary, ECAFE	"
Mr. U. Yun, Chief, Industry & Trade Division, ECAFE	"
Mr. H. A. Pilapil, Chief, Cottage & Small Scale Industries, ECAFE	"
Mr. E. Gergely, Consultant on Leather Industry, ECAFE	"
Mr. Ansar Khan, Information officer, ECAFE	"
Mr. P. Toutchkor, Interpreter, ECAFE	"
Mr. Tran Phu, ECAFE Secretariat	"
Mr. C. Subramaniam, Minister for Finance, Government of Madras	"
Dr. P. S. Lokanathan	"



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