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Bulletin of The
CLRI Madras

Mar 1961

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Bulletin of
The Central Leather
Research Institute
Madras



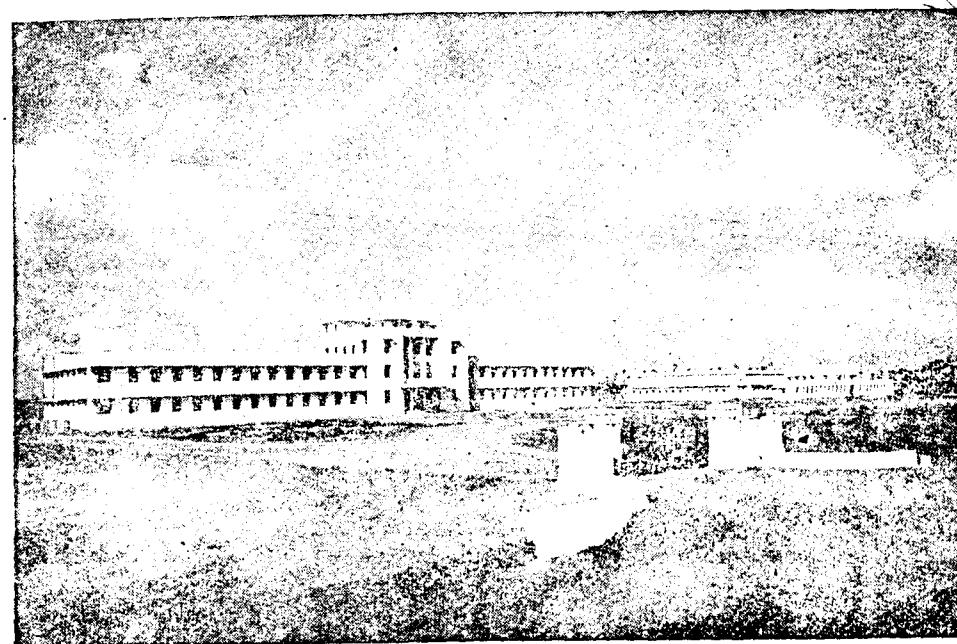
Vol. VII

MARCH, 1961

MADRAS

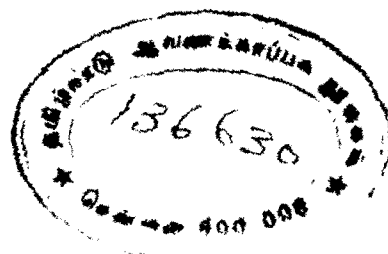
No. 8

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COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH
INDIA

Bull. cent. Leath. Res. Inst., Vol. 7, No. 8, Pp. 351-402. Madras, March, 1961



Bulletin of The Central Leather Research Institute

Vol. VII MARCH, 1961 No. 8

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The Bulletin of the Central Leather Research Institute is issued monthly.

Communications regarding contributions for publication in the Bulletin, books for review, subscriptions and advertisements should be made to the Managing Editor, C. L. R. I., Madras-20.

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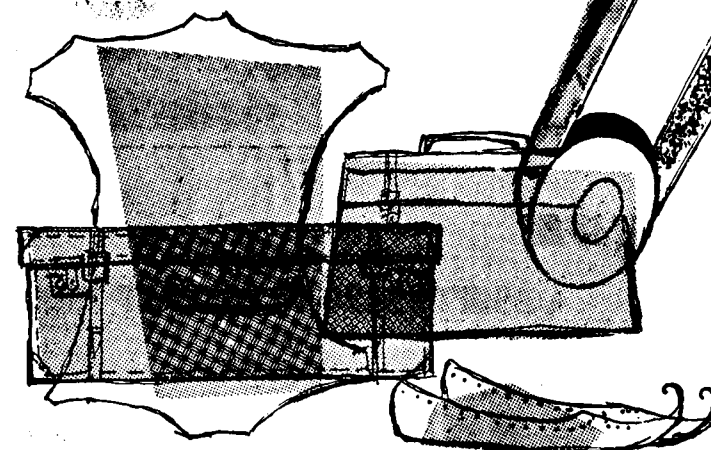
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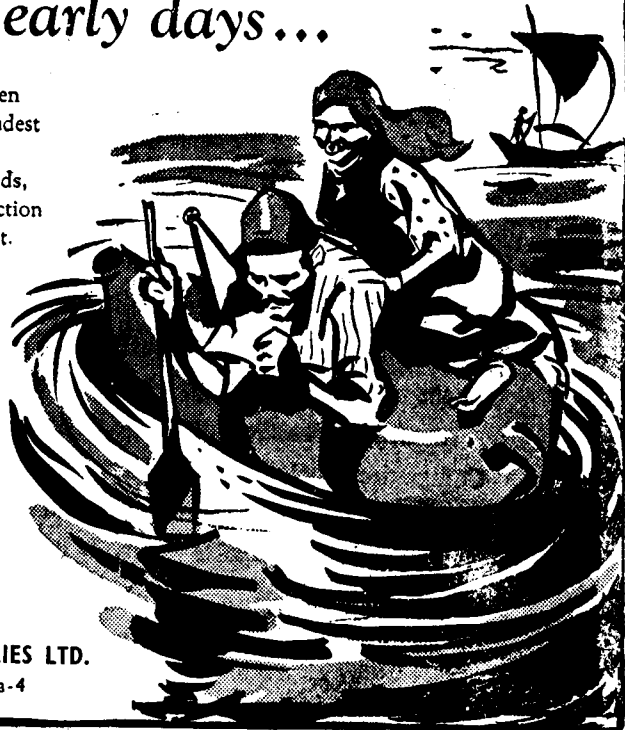
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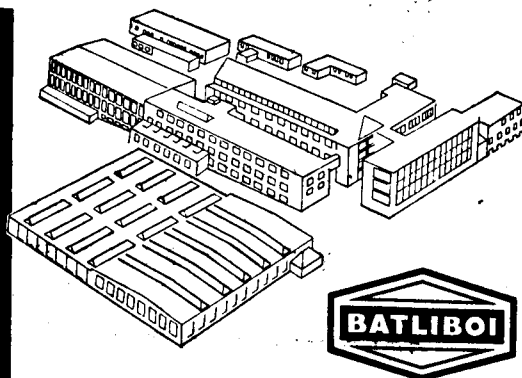
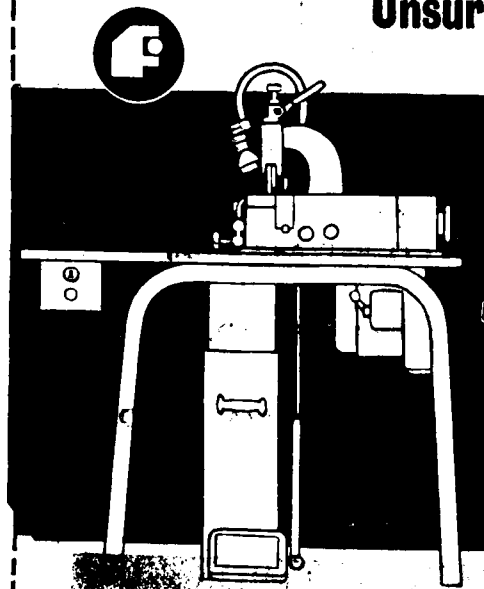


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NEUTRALISATION OF CHROME TANNED LEATHER*— PART I

BY

K. S. JAYARAMAN & Y. NAYUDAMMA
Central Leather Research Institute, Madras

SUMMARY

A study on the use of salts of certain organic acids as neutralising agents has been made with chrome tanned hide powder and pelt pieces by adjusting to different pH levels. The effect of concentration of the salt on the removal of protein bound acid has been pointed out. The ionisation constant of the organic acid and the buffering capacity of the salt seem to influence the degree of neutralisation.

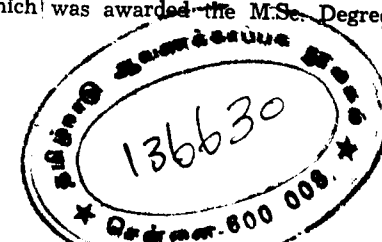
Introduction

Neutralisation of chrome tanned leather, an essential operation before dyeing and fatliquoring, consists of (i) rinsing in running water to remove free acid and uncombined chrome tanning material, (ii) treatment with a mild alkali to neutralise the remaining acid and (iii) final washing to remove the soluble salts formed during neutralisation. The slightest variation in the procedure or the type and amount of alkali used have far reaching effects on the finished leather.

In neutralising, both under-neutralisation as well as over-neutralisation are to be avoided and the undesirable acidity should be removed without unduly disturbing the stable chrome complex in the leather.

It has been recognised that there are three possible types of acidities in chrome leather, viz., (i) acid combined with the hide substance, (ii) acid complexly bound to fixed chrome and (iii) acid ionically bound to fixed chrome. Various methods have been suggested in the past^{1, 2, 3} to distinguish between the various types of acidities. Though it is not possible to estimate separately the ionically and complexly held acids, the protein bound acid has been estimated accurately by the method suggested by

* Based on K.S.J.'s thesis (1958) which was awarded the M.Sc. Degree of the Madras University.



Nayudamma.⁴ In the process of neutralisation, it would be profitable if only the undesired free and protein bound acids are neutralised uniformly throughout the leather without altering the complex to any great extent. Furthermore, the neutralisation process has also to be adjusted according to the type of leather to be produced and nature of tanning given. For judging the degree of neutralisation bromocresolgreen has been suggested by Otto⁵ as the best indicator.

A study of the behaviour of common neutralising agents such as sodium and ammonium bicarbonates, borax, Na silicate, ammonia, etc.^{6,7,8,9} has been made in the past and the better neutralising action of ammonium bicarbonate has been explained by Theis *et al.*¹⁰ as due to its greater and uniform penetrating characteristics.

From the studies of certain salts of organic acids, it was recognised that the neutralising power of an agent was not in direct relationship to the alkalinity of the solution. The differences in the behaviour of different neutralising agents have been explained by Otto⁵ to be due to varying degrees of complex-forming tendencies of the anions. The fatliquoring and dyeing properties of leather are to a great extent influenced by the nature of neutralising agent. It has been shown previously that salts of certain organic acids help in producing more level and uniform dyeing and help in achieving better retanned leather by altering the highly cationic surface charge of chrome leather.

The present study relates to investigations on the changes of the nature of chrome complex, the advantageous removal of protein bound acidity from the system, the effect of the chrome complex after neutralising, on the thermal stability, dyeing and fatliquoring properties of the leather and the physical characteristics of the leathers produced when salts like acetate, oxalate, phthalate and adipate are used as neutralising agents.

In part I of the study, the amount of neutralising agent required to obtain different degrees of neutralisation and its effect on the protein bound acid are discussed.

Experimental

Preparation of leather and chrome tanned hide powder:

About 300 pieces of dehydrated and dried pelt were soaked in 8% sodium chloride solution overnight. Next day, the solution

was drained off and 4% salt was added. About 1000 gm. of hide powder were soaked in water containing 4% salt and drummed. When the pelt pieces were completely soaked back, the tanning was done simultaneously with both pelt and hide powder. Chrome liquor (reduced with sulphur dioxide) was added to the drum in instalments and the tanning was carried over a period of three days with an amount of chrome liquor such that the final tanned powder contained 7.5% Cr₂O₃ on hide substance basis. The final pH was adjusted to be 3.0. After attainment of equilibrium, the excess chrome liquor was squeezed out and the chromed powder/pelt washed in three to four changes of distilled water adjusted to the final equilibrium pH. The powder was then squeezed, dried, ground in a Wiley mill, bottled air tight and taken up for the study. The tanned pieces were kept corked separately in a bottle for shrinkage temperature studies.

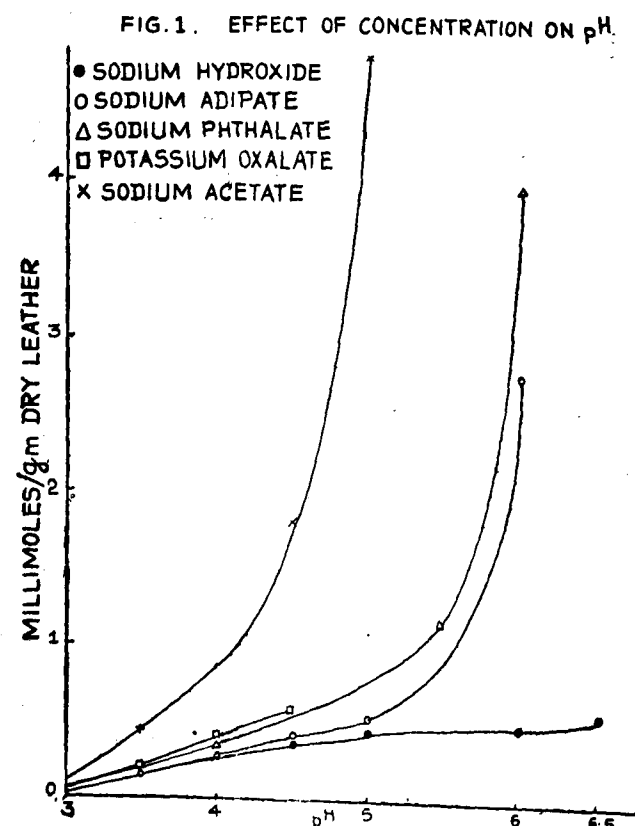
Three strips of chrome tanned pelt and sufficient amount of chromed hide powder were used so that the material contained 10 gm. of hide substance in each case. The stock was put in beakers, wetted back with a few drops of octyl alcohol and 400 ml. of water and the pH adjusted with the salts of acetic, oxalic, adipic and phthalic acids. The pH range 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5 and 7.0 was covered noting the exact amount of the different neutralising agents needed to attain and maintain a given equilibrium pH. A control was also run by adjusting the pH with NaOH. In the case of vegetable tannins, the powder and pelt were treated with 1%, 3%, 5%, 10% and 15% of tannins. In this case, the pH was not adjusted, the change in pH only being noted.

Results and Discussion

As the neutralising agents under study are not alkaline like NaHCO₃, large amounts were required to attain pH values above 5.0. With oxalate, the pH value which was initially adjusted to 4.5 and to 5.0 gradually rose upto 6.5 and 7.5 respectively. Hence the range 4.5 to 6.0 could not be covered with oxalate. After equilibrium was attained, the pieces were taken up for T₁ studies and the neutralised powder was filtered, pressed, dried, ground in a Wiley mill and analysed for Cr₂O₃, protein bound acid, hide substance, moisture, complexly held sulphate and basicity.

The differences in the behaviour of the different neutralising agents can be studied by estimating the amount of any particular neutralising agent needed to attain a particular pH and the acid bound to the protein at that pH. When the amount of neutralis-

ing agent expressed as millimols/gm. dry leather is plotted against the pH to which the leather is neutralised (Fig 1), the amount of neutralising agent needed upto pH 5.0 increased in the following order (i) adipate, (ii) phthalate, (iii) oxalate and (iv) acetate.

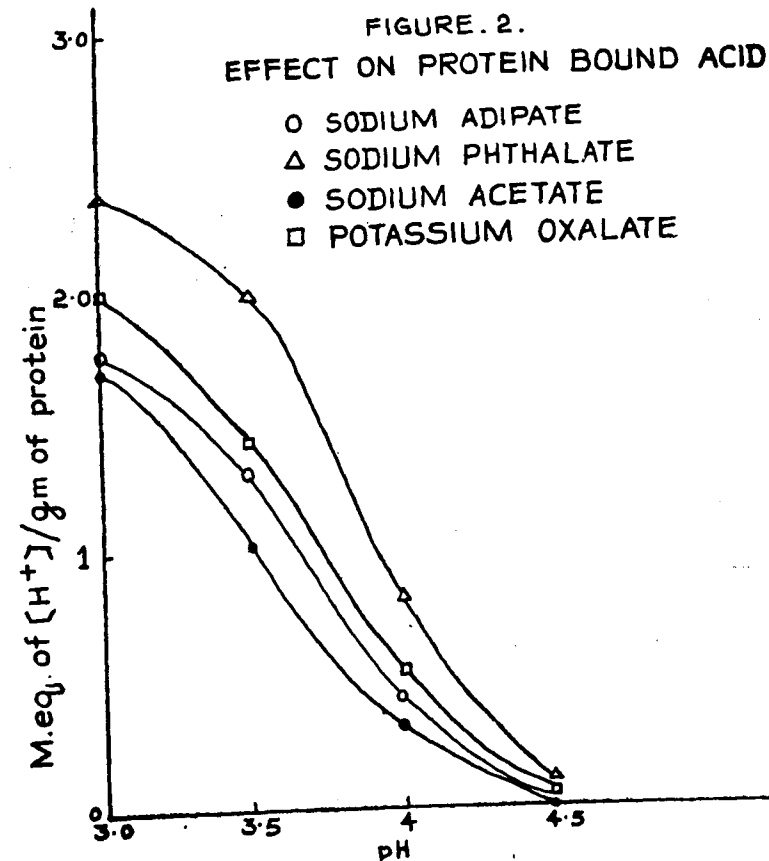


It is clearly seen from the values that the amount of these neutralising agents required to attain to any particular pH is comparatively high as compared to the customary neutralising agents studied by Theis *et al.*¹¹ on similar lines. This difference in the behaviour of salts of organic acids is due to the fact that bicarbonate or borax is alkaline in nature and a direct neutralisation of the acid is achieved. In the case of organic salts, neutralisation is only due to their buffer action. These salts possess the advantage, that any error on the part of the tanner, by way of adding larger amounts does not affect the pH appreciably and that over-neutralisation is not effected.

The amount of neutralising agent required is controlled by the degree of buffering and the pH range at which maximum buffer

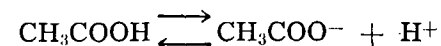
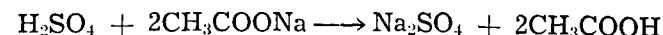
action occurs. From figure 1, it is observed that acetate exerts its maximum buffer action at the pH range 4.5 and phthalate and adipate at pH 5.5 and 6.0 respectively.

The peculiar behaviour of oxalate for which the curve could not be traced in the pH range 4.5-6.5 could be explained as follows: at the concentration of oxalate employed to obtain pH values above 4.5, the oxalate ion displaces the complexly held OH groups and the pH of the system goes up, like the rise in pH observed by Thorstensen and Theis,¹² on addition of potassium oxalate to chrome liquors.



The efficiency of the neutralising agent must be judged from the amount of acid removed at any particular pH. With this object, m.eq.acid/gm. protein in the leather has been plotted against the pH of neutralisation (Fig. 2). It is observed from the figure that sodium acetate neutralises better than the others though the amount of acetate required is high. Assuming the

acid bound to the protein to be sulphuric acid, a reaction of the type given below can be expected.



Acetic acid formed is a weak acid and ionises only to a small extent and the dissociation is further suppressed due to the presence of the salt and hence the decrease in the $[\text{H}^+]$ of the system. The neutralisation proceeds in a similar manner at various pH values. The acid that is bound to the protein gives a lower or higher value depending upon the organic acid and dissociation constant of the acid. The following is the decreasing order of dissociation constant: adipic, phthalic, oxalic, acetic (pK_2 values for the dicarboxylic acids being taken into consideration). It is also observed that the protein bound acid is completely removed at pH 4.5 and at higher pH values the rise in pH is due to the pH of the solution of the salt itself which is slightly alkaline in nature. In case of NaOH alone, direct neutralisation of the acid is achieved and hence lesser amount is required for any equilibrium pH.

Hence the neutralising action of any particular salt of organic acid depends upon (i) ionisation constant of weak acid and (ii) its buffering capacity. As the protein bound acid is completely removed at pH 4.5, the neutralisation process can be carried along with tanning itself by finishing at a pH 4.5; this method has been tried with success by the addition of salts of certain organic acids to chrome liquors in the final stages of tanning and completing the tanning at pH 4.5.

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NEUTRALISATION OF CHROME TANNED LEATHER*— PART II. EFFECT ON THE ACIDITY AND BASICITY OF THE COMPLEX

BY

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Central Leather Research Institute, Madras

SUMMARY

The overall basicity of chrome tanned hide powders neutralised to various degrees by salts of different organic acids has been studied and the need to take into account the protein bound acid or base depending upon the pH condition of final leather, in calculating the basicity of the complex has been pointed out.

In the process of neutralisation, the acidity and basicity of the chrome complex as well as of the protein-chrome compound may change apart from the removal of protein bound acid. The traditional method of calculating basicity of chrome complex in chrome leather, viz. by subtracting the sulphato acidity from 100 is erroneous in the case of chrome complexes containing anions other than sulphate. Hence the method suggested by Thorstensen and Theis¹ has been adopted and the basicity measured directly. This basicity figure represents the overall basicity. It has to be pointed out here that a distinction should be made between the basicity of the leather and the basicity of chrome complex. Acid or base is likely to be bound both to the protein and to chrome and the basicity of the chrome complex alone may be calculated as follows:

$$\begin{aligned} \text{Basicity of the chrome complex} &= \text{overall basicity} + \\ &\quad \text{protein bound acidity} \\ \text{or} &= \text{overall basicity} - \\ &\quad \text{protein bound basicity} \end{aligned}$$

This method of estimating the basicity of the chrome complex has been utilised to calculate penetration capacity of different

* Based on K.S.J.'s thesis (1958) which was awarded the M.Sc. Degree of the Madras University.

anions and the degree of complexing by these anions as follows:

$$\text{Overall acidity} = 100 - \text{overall basicity}$$

$$\text{Acidity due to organic ion} = \text{overall acidity} - (\text{Protein bound acidity} + \text{sulphato acidity})$$

The sulphato acidity was determined by cooking the chrome tanned leather neutralised with organic salts, with sodium dihydrogen phosphate after neutralising the protein bound acid by KCl titration. Using these methods, the acidity and basicity of the leather have been calculated and the data so obtained are presented in this paper. (Fig. 1 and Table I)

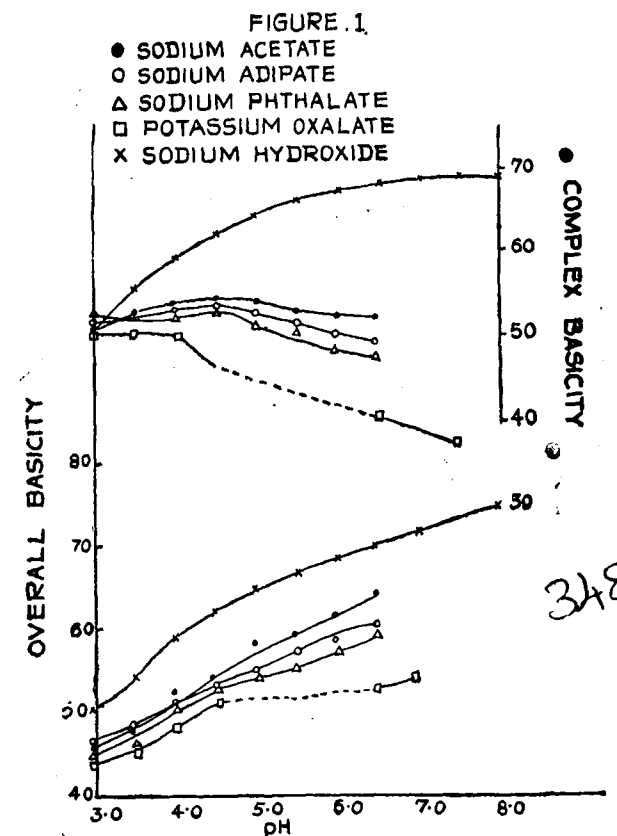
Results and Discussion

In the case of neutralisation with sodium hydroxide, part of the alkali is used up in neutralising the protein bound acid and the rest enters the complex. Hence the gradual rise in basicity upto 66% at pH 5.5 beyond which it is not affected much. The complex seems to be sufficiently stable so that alkali which is further added, is bound to the protein to a greater extent, penetrating the complex only to a small degree.

A similar rise in overall basicity is observed in the case of salts of organic acids at all pH values, though no OH ion is introduced into the system. At pH values less than 4.5, the protein bound acidity interferes with the determination of overall basicity and the basicity of the complex obtained by adding protein bound acidity to overall basicity remains more or less constant within experimental errors.

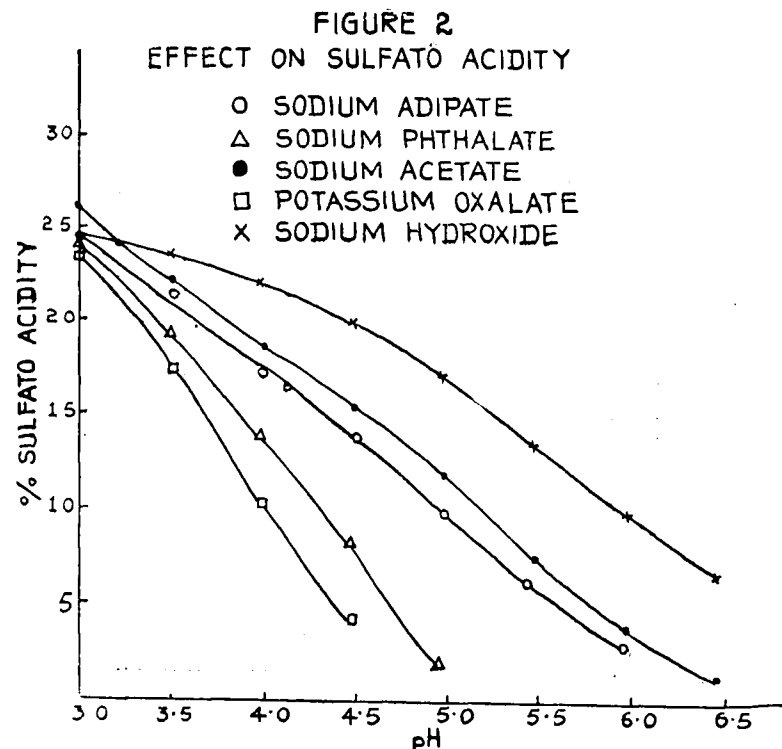
At pH values above 4.5 also where there is no protein bound acidity, a similar rise is observed. This rise in basicity values would be due to (i) increase in —OH or (ii) decrease in Cr_2O_3 (Lehigh basicity is expressed as m.eq. OH/m.eq. Cr_2O_3). But no additional —OH groups have been introduced; also it has been observed that these neutralising agents exert a stripping action above pH 4.5; so it is possible that anionic complexes of poor tanning property containing no —OH groups are removed from the leather. The assumption that rise in the overall basicity is due to the stripping of chrome seems to be justified for the basicity remains very nearly the same at all pH values when calculated on original chrome content.

When oxalate is employed as a neutralising agent, the overall basicity remains constant upto pH 4.5 and is found to be higher at higher pH values 6.5 and 7.5. As explained earlier, it should be due to the drastic stripping of chrome by oxalate.



There are two possible ways by which the —OH groups may be bound in the leather at pH values higher than 4.5, i.e. (a) complexly bound to chrome and (b) bound to the protein. For finding the basicity of the chrome complex, a correction could be applied by a back titration to pH 4.2 and such figures are given in the table. It is seen from the values that the complex basicity falls with increase of pH and the fall is characteristic of the penetrating power of the anion. The order is as follows: oxalate > phthalate > adipate > acetate. Though there is some displacement of OH groups by adipate and phthalate, this is small as compared to that with oxalate which accounts for a drastic rise in pH of the system when oxalate is used as a neutralising agent.

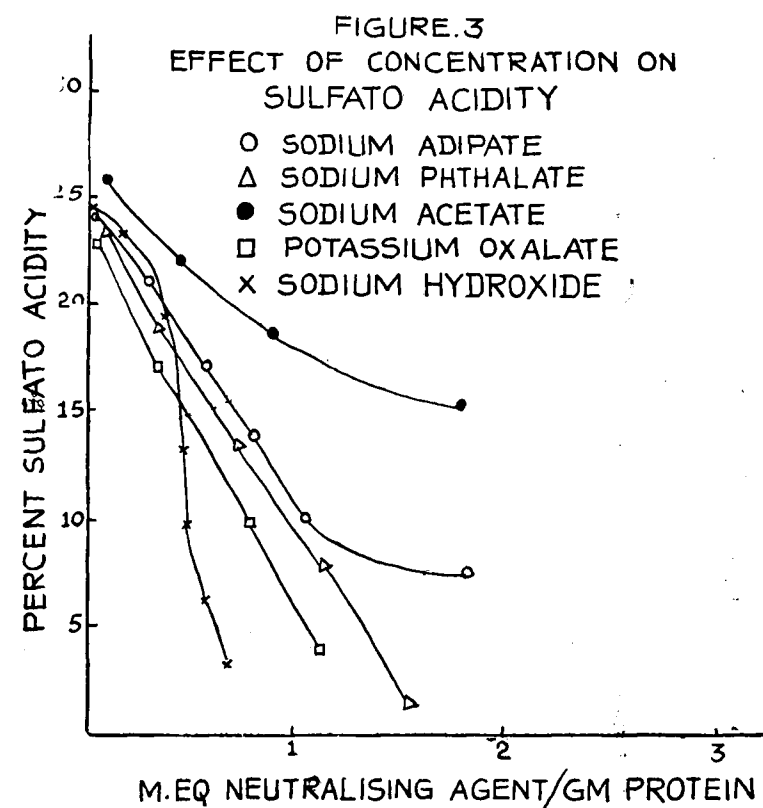
As explained earlier, the penetration capacity of the various anions has been calculated from overall basicity values. The penetrating characteristics of an anion are to be judged not only with respect to pH but also with respect to the ionic concentration required to attain any particular pH. When sulphato acidity is plotted against concentration of the neutralising agent (fig. 3), it is seen that at any particular concentration, the ability to displace the sulphate ion from the complex is in the following order:



acetate < adipate < phthalate < oxalate < OH⁻. When percent sulphato acidity is plotted against the pH of neutralisation (fig. 2), the ease of replacement of sulphato groups bound to the chromium complex, at a particular pH is in the following order: OH⁻ < acetate < adipate < phthalate < oxalate. The findings are in agreement with those of Theis and Meerbott² who showed a drastic reduction in combined sulphate with addition of sodium oxalate to chrome liquor as compared to addition of formate and acetate.

Though sodium hydroxide is shown to be the most penetrating in fig. 3, it is seen that sulphato groups resist replacement in

case of sodium hydroxide neutralisation until a higher pH (6.5) is attained. The reason for this is quite clear when the ionic concentrations required to attain any particular pH are taken into consideration. For example, for attaining a pH value of 4.5, 0.38 m.eq. of NaOH per gm. dry leather is required as compared to 1.8 m.eq., 1.2 m.eq., 0.80 m.eq., and 0.58 m.eq./gm. dry leather in the case of acetate, phthalate, adipate and oxalate respectively.



It is also possible that the OH ion is not available for penetration into chrome complex since it is bound as protein bound base above pH 5. The results obtained agree with those of Theis *et al.*² who showed a greater drop in sulphato acidity with NaHCO₃, borax and phosphate than with sodium hydroxide. Similarly, though the ionic concentration required to attain pH 3.0-3.5 is the same in the case of adipate and phthalate, the drop in sulphato acidity is more with phthalate due to the better penetrating characteristics of phthalate ion.

TABLE I
Effect on Basicity

pH	Adipate			Phthalate			Oxalate			Acetate			Sod. hydroxide		
	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
3.0	46.4	51.9	—	44.9	52.6	—	44.3	50.5	—	45.4	51.1	—	46.9	50.3	—
3.5	48.5	52.3	—	46.2	52.7	—	45.7	50.4	—	47.5	50.8	—	54.3	55.5	—
4.0	51.0	52.3	—	50.8	53.3	—	48.2	49.3	—	52.5	53.8	—	58.9	59.9	—
4.5	53.2	53.4	—	53.0	53.3	—	51.6	46.2	—	54.2	54.2	—	62.2	62.9	—
5.0	55.1	52.8	—	53.8	51.4	53.5	—	—	—	58.5	54.1	54.5	65.0	64.3	—
5.5	57.6	51.3	55.5	55.2	50.9	53.8	—	—	—	59.2	53.0	55.7	67.0	65.9	—
6.0	58.2	50.0	54.7	57.6	48.2	52.7	—	—	—	61.8	52.3	53.7	68.8	67.2	—
6.5	60.5	49.2	54.1	59.3	47.3	53.7	53.0	40.4	33.4	64.5	52.0	54.2	70.3	68.0	—
7.0	—	—	—	—	—	—	—	—	—	—	—	—	71.8	68.5	—
7.5	—	—	—	—	—	—	54.8	34.7	24.8	—	—	—	73.0	69.0	—
8.0	—	—	—	—	—	—	—	—	—	—	—	—	74.5	69.0	—

a = Overall basicity. b = Basicity of the complex. c = Overall basicity (on original chrome content).

It is observed that though there is a reduction of sulphato acidity in the pH range 3-5, the fixed chromium is not affected. However, at higher pH values there is a decrease in fixed chromium due to the formation of complexes of oxalate, adipate, phthalate or acetate which have varying degrees of stability and tanning potency; these in turn affect the stripping process.

It is also observed that the thermal stability is not influenced to any great extent by the sulphato acidity and it appears that the thermal stability is influenced more by the nature of other ligands which have entered into the chrome complex.

Conclusions

The overall basicity determined by the Lehigh method is of help in calculating the penetration characteristics of the different anions. The basicity of the complex and the basicity of the leather may not be the same except at the isoelectric point at which neither acid nor base is bound to the protein. At all other pH values, the acid or base bound to the protein must be taken into consideration for calculating the basicity of the complex. The anions of different neutralising agents penetrate into chrome complex displacing sulphato groups; the extent of this depends upon the nature and concentration of anion which forms complexes of different charge, stability and tanning properties. When such agents are used to a great extent, undesirable reactions like stripping of chrome may follow; but when used in reasonable amounts, much stabler complexes are formed which result in improved properties in the finished leathers.

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RESEARCH BEARS FRUIT

Manufacture of chrome retan leather*

BY

A. GANESAN, S. P. GHOSH & S. M. DE

Introduction

Three processes for manufacture of chrome retan leather were demonstrated recently at Calcutta. The first of these (Process I†) has been described earlier. The other two are described below:

PROCESS No. II

Raw materials:

8 wet salted cow hides (130 lb., i.e., 58.96 kg.) from Raja Bazar Market, Calcutta, were employed.

As in Process I†, soaking was in plain water, liming was with a liquor containing sodium sulphide, ammonium sulphate and lime and deliming was with ammonium sulphate. The fleshed weight was 150 lb. (68.04 kg.).

Pickling:

Pickling was done with the following chemicals:

2% sulphuric acid (sp. gr. 1.4)

6% common salt

70% water.

The hides were drummed in the pickle bath for 2 hours and left well immersed overnight.

Chrome tanning:

The running period was the same as in Process I during chrome tanning. Instead of using prepared chrome liquor 7%

* Process demonstrated during the period December 1960 and January 1961, in Messrs. Hindustan Tannery, Dhapa, Calcutta.

† For details of Process I, reference may please be made to *Bull. C.L.R.I.* 7, 320 (1961).

B & C chrome extract powder was added. The pH of the exhaust chrome bath was brought to 3.4 with the addition of 1% sodium bicarbonate. One half of the quantity of the alkali was added along with the chrome liquor itself, the balance being added after running the drum for 5 hours.

Rechroming:

The shaved leathers were rechromed for 1 hour in the drum with stock chrome liquor (described earlier) equivalent to 2½% bichromate (on fleshed weight) and 1% sodium bicarbonate (on shaved weight) without using any float. The chrome liquor was completely absorbed by the leathers. The hides were flooded with 100% water. ½% sodium bicarbonate was added into the drum and the drum run for ½ hour. Again ½% sodium bicarbonate was added slowly over a period of ½ hour, the pH being raised to 4.3.

Neutralisation:

As in Process I, neutralisation was done with 12 oz.% sodium bicarbonate and 200% float.

Fatliquoring:

This was done with the following:

2¼% sulphated pungam oil (highly sulphated) or 2½% sulphated fish oil

2¾% free fish oil

100% cold water.

Fatliquoring was carried out for 45 minutes.

Retanning:

Retanning was done with a mixture of 6% cutch extract No. II and 4% kenmosa spray dried extract (taken on shaved weight), the procedure being the same as in Process I.

Refatliquoring:

After retanning, refatliquoring was with the following:

1½% sulphated fish oil

½% free fish oil

¼% tallow

50% water.

The subsequent mechanical operations, viz., samming, drying, conditioning with saw dust, staking, shaving, trimming, buffing, snuffing and restaking were carried out as in Process I.

Finishing:

Instead of linseed mucilage, the following coat was applied on the grain:

6 oz. (0.16 kg.) sulphated fish oil
3 oz. (0.08 kg.) kerosene oil
1½ oz. (0.04 kg.) kid oil
water to make 2 litres.

The pigment season was applied in the same way as in Process I and then the leathers were dried.

Area: 181 sq. ft.

Average area per piece: 22.6 sq. ft.

PROCESS No. III

Raw materials:

9 wet salted cow hides (154 lb., i.e., 69.85 kg.) from Raja Bazar Market, Calcutta, were taken.

As in Processes I & II, soaking was in plain water, liming was with a liquor containing sodium sulphide, ammonium sulphate and lime and deliming was with ammonium sulphate. The fleshed weight was 190 lb. (86.18 kg.). Pickling was done in the same way as in the previous processes, i.e., with a mixture of sulphuric acid and common salt.

Chrome tanning:

This was done as in Process II, but the bichromate content of liquor was 4.5%. The pH of the exhaust bath after basification was 4.5. The shaved weight was 90 lb. (40.82 kg.). The shaved leathers were assorted according to their texture.

Rechroming for the looser sides:

Looser sides were rechromed with the prepared chrome liquor equivalent to 1½% bichromate (on pelt weight) mixed with 1% sodium bicarbonate (on shaved weight). The exhaust pH was 4.6.

Neutralisation:

The leathers were neutralised with 5 oz.% sodium bicarbonate and 200% water. The stock was left overnight in the drum. The tighter leathers were neutralised with 10 oz.% sodium bicarbonate in 200% float, running ½ hour and leaving them overnight in drum. The extent of neutralisation was the same as in the previous process.

Fatliquoring:

The leathers were fatliquored with the following:

2% sulphated pungam oil
(highly sulphated)

2% sulphated fish oil	{ or }	3.0% sulphated fish oil
1% raw fish oil		1.0% free fish oil
0.5% kerosene oil		0.5% kerosene oil
100% cold water		100% cold water

The goods were drummed with the above fatliquoring composition for 25 minutes.

Retanning:

Retanning was done with the following:

10% cutch extract
100% total float.

The cutch extract was added in three instalments at intervals of ½ hour. The drum was further run for ½ hour after the last addition of extract. Then 5.0% salt was added, dried and the drum run for another 15 minutes. The bath was then drained. The sides were given three washes for 15 minutes each in 200% float.

Refatliquoring:

The leathers were refatliquored with the following:

1½% sulphated fish oil
0.5% free fish oil
0.25% tallow
0.50% kid oil
60% cold water.

The goods were drummed by the above composition for 15 minutes.

Dyeing:

This was done with the following composition:

3 oz.% dye
3 oz.% acetic acid
100% water.

The goods were drummed with the above composition for 15 minutes.

The drying and other operations were carried out as in the earlier processes.

The leathers were finished as per recipe in Process I.

Total area: 225½ sq. ft.

Average area per piece: 25 sq. ft.

Total wet salted weight of three processes: 505 lb. (229.06 kg.)

Total area	-do-	: 605½ sq.
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Average area per piece	-do-	: 24.2 sq.
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TECHNICAL SEMINAR

Studies on oil tannage*

BY

K. S. JAYARAMAN

The data obtained on a chromatographic study of the oxidation products obtained from fish oil were presented and it was shown that acrolein and/or crotonaldehyde and glyoxal were the main aldehydic products. A separation of acrolein and crotonaldehyde was not possible. The possibility of these aldehydes getting fixed to the protein was also indicated.

The birefringence properties of oil tanned fibres indicated that some types of cross links similar to those present in formaldehyde or in Cr tanned leather were formed during oil tannage also. In the light of some of the earlier findings, it was suggested that the cross links formed might be through the aldehydes formed during oil oxidation.

The isoelectric point of oil tanned and formaldehyde-oil combination tanned leathers indicated that the lowering of I. E. P. (4.7—4.8) might be due to the blocking of $-NH_2$ groups, probably by the aldehydes and introduction of additional carboxyl groups through the fatty acids formed during the tanning.

The characteristic physical properties of chamois leathers, such as, easy and high water absorbancy, stretchiness, low density etc. have been found to be improved after an alkali wash as compared to solvent extraction of oil tanned leather. This difference in property has been suggested to be due to the insoluble components formed during tanning, during the alkaline wash.

* Summary of talk given on February 10, 1961.

TECHNICAL SEMINAR
Australia's livestock Industries*

BY

P. J. SKERMAN

Australia has 152 million sheep, 16 million cattle of which 3 million are dairy cattle and 1¼ million pigs.

Australia has long been famous for its sheep and some 85% are Merino wool producing sheep. The Merino thrives in the dried lower rainfall areas usually under 20 inches of rain and most of Australia's wool is produced from natural grass. Queensland's merino wool is raised mostly on heavy black cotton soils growing michell grasses (*Astrelba spp.*). There is little shade and under hot conditions, ram fertility is affected. Hence mating is usually arranged for the cooler months. Another important area is the mulga scrub country. Mulga is an *Acacia* (*A. ancura*) which is edible. The wood is a familiar tourist souvenir made up as boomerangs, book-ends etc. In a drought the mulga is rolled down by bulldozer so that the sheep can eat the leaves within reach. The cattle eat the higher leaves. Grass seed is planted at this time so that a new pasture can be established.

In the mitchell grass downs areas droughts can be severe. Dr. Skerman is working at Queensland University studying the growth of *Sorghum* (jowar) on these heavy soils under dry farming conditions to conserve the jowar underground as silage for drought feeding. This has been very successful. Fat lambs are produced in the better rainfall areas usually receiving over 25 inches of rain but not more than 40 inches. Irrigation areas also raise fat lambs on improved temperate type pastures, such as, rye-grasses and clover. The fat lamb is usually sired by an English Downs breed ram from a Border-Leicester-merino cross ewe. Fat lambs are sold at 3½-4 months at a dressed weight of 28-35 lb.

* Summary of talk given by Prof. P. J. Skerman, M.B.E., D.Sc., Q.D.D., Queensland University and United Nations Expert to Kenya Government, on 27-2-1961.

Goats are not used very much now. Some small suburban herds are kept for home milk supply and these are usually of the Swiss Scanen breed. In dry Western Queensland, goats were kept for milk but they so quickly denuded the areas of vegetation that they are now being destroyed and bottled pasteurised milk is distributed in refrigerated railway carriages.

The beef cattle industry in Australia is largely migratory. Cattle are bred in the North of Queensland, and the Northern Territory and Western Australia and move to South and East to better areas for fattening and slaughter. Fattening is carried out on natural spear grass (*Heteropogon contortus*) pastures which are burned annually in September and the new growth fattens from December to April, or the cattle are fattened on crops, such as, oats or *Sorghum* (jowar) or irrigated pastures. Ticks are a problem and severely damage the hides of infested cattle. Tick-free hides bring 1/8 in Queensland, but ticky hides only return 1/3 (1 rupee = 2/- Australian approx.). The ticks have become progressively resistant to arsenic, DDT and gammexane (BHC) and now diazinon is being tried. The Commonwealth Scientific and Industrial Research Organisation (C.S.I.R.O.), the Universities and the State Department of Agriculture Stock are carrying out a good deal of research in tick control; a load of 20 ticks reduces an animal's live weight by 90 lb. in a year. Queensland introduced some Brahman blood to cross with British breeds to increase heat and tick resistance. It has been found also that Brahman animals can utilise grass with protein content as low as 4% whereas British breeds can utilise it only down to 5% protein.

Stud cattle are very costly in Australia. The champion Hereford Bull at the 1959 Brisbane Royal Show was sold for A £ 6500 (65,000 rupees).

A good deal of work has been done on pastures and soil fertility. The poor low-lying sandy soils of coastal Queensland have been found to need 5 cwt. P₂O₅, 1 cwt. K₂O, 5 cwt. CaCO₃, 14 lb. MgSO₄ and 7 lb. each of boron and molybdenum. At present, we cannot afford to apply this amount.

Queensland has 23 million acres of another *Acacia* scrub called brigalow (*Acacia hoopophylla*). This was heavily infested with a cactus (prickly pear) in 1926 so that the Lands Department values it at nil per acre. A scientist was sent to the Argentine

and he brought back a moth (*Cactoblactis cactorum*) the caterpillar of which completely eradicated the cactus in three years. Now, some of the best farms in Queensland exist on previous prickly pear land and a Memorial Hall has been built in honour of the caterpillar.

The brigalow scrub is being pulled down with bulldozers and chains, burnt and sown with grass from the air or cultivated and is now very productive.

A team of 14 Indian Veterinary science graduates visited Australia in 1959 to study sheep and wool and Dr. Skerman took them for a 2000 mile conducted tour by bus through Western Queensland.

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CLASSIFIED ABSTRACTS

CHROME TANNAGE

The production of suede leather.

E. Luescher, *Australian Leather Journal, Boot and Shoe Recorder*, 63, No. 6, 127-134 (1960). Calf, goat and sheepskins and to an increasing extent splits are used for the production of suede leather. Factors that are held important for processing suedes are an open fibre structure, a uniform cationic chrome tannage and a fatliquoring that ensures good dyeing yielding a dry fibre structure with good buffing properties.

Two processes are described for the chrome tanning of skins for suedes—one for goods that are assorted in the limed condition and the other after chrome tanning. A 'dry' chrome tannage involving the use of cationic oils in the chrome bath is preferred. Similar tanning procedures are given for splits also.

The requirements for good suede-dyeing are levelness of shade, sufficient penetration and good buffing fastness. Procedures are described as to the best way of achieving these properties.

The raw materials, tanning techniques and dyeing procedures followed for clothing suedes are also described. Use of chrome stearato chloride for showerproofing and the Dena fast dyestuffs helps in the production of suedes that are showerproof and fast to modern dry cleaning methods. Cationic fixing agents help to improve the wash fastness of such dyeings.

Use of oil-in-water silicone emulsions for showerproofing and a fluorine hydrocarbon product under the name 'Scotch guard' for anti-soiling effects is also mentioned.

P. S. V.

TESTING

Titration curves of colloidal surfaces. III. Wool.

Milton B. Engel and Norman R. Joseph (Univ. of Illinois, Colleges of Dentistry and Pharmacy, Chicago, Illinois) *Arch.*

Biochem. Biophys. **86**, 117 (1960). By studying colloidal charge density at various pH levels, titration curves of wool surfaces were determined. Samples were studied at water content of 50-55%. At or below this level, potentials were independent of electric resistance and of water content, and also of the weight of sample. Normal Donnan potentials were measured and Donnan ratios estimated. Colloidal charge densities were calculated from Donnan ratios. Dilution potentials were calculated from the Donnan ratios and standard values of ion conductances. The calculated values agreed with measurements of the dilution potential. From the dilution potentials at various pH levels, colloidal charge densities were estimated. A low concentration of picric acid was found to displace the titration curve as determined in solutions containing chloride as the only other anion. The displacement was toward higher pH; the magnitude was from 1 to 2 units. Similar effects have been found in connective tissues. The titration curves were compared with those determined for whole fibres measured independently.

On light-scattering studies of isoionic proteins.

Serge N. Timasheff and Bernard D. Coleman (The Sterling Chem. Lab., Yale Univ., New Haven, Connecticut and The Eastern Reg. Res. Lab., Philadelphia, Pennsylvania) *Arch. Biochem. Biophys.* **87**, 63 (1960). The calculations described here show that, in light-scattering studies on isoionic proteins, the attractive force due to charge fluctuations results in a considerable contribution to the derivative of the excess chemical potential of the protein with respect to its concentration in the presence of salt as well as in the salt-free case. This attractive force is sometimes sufficient to contribute significantly to the negative values of the slopes of light-scattering plots even in the case of proteins which carry a nonvanishing mean electric charge from ion-binding. Thus, it appears that the interaction of fluctuating charges provides at least a partial explanation for the negative slopes often observed in light-scattering experiments on isoionic proteins in the presence of salt.

Paper chromatography of saturated, unsaturated and hydroxy fatty acids.

Vladimir P. Skipski, Stuart M. Arfin and Maurice M. Rapport (Div. of Expl. Pathology, The Sloan-Kettering Insti. for Cancer Res. and Depart. of Biochem., Albert Einstein College of Medicine,

Yeshiva Univ., New York), *Arch. Biochem. Biophys.* **87**, 259 (1960). Methods are presented for separating straight-chain saturated, unsaturated, and 2-hydroxy fatty acids from C_{14} to C_{24} by paper chromatography and for detecting the acids as bismuth sulfides. These methods are applied to the analysis of fatty acids isolated from bovine spleen glucocerebroside and bovine spinal cord galactocerebroside.

Detection of some deoxy sugars and aldehydes using thiobarbituric acid

L. D. Saslaw and V. S. Waravdekar (The Biochem. Branch, Armed Forces Inst. of Pathology, Washington, D.C.) *Arch. Biochem. Biophys.* **90**, 245 (1960). Some aldehydes may be visualized on filter paper with the use of a thiobarbituric acid reagent. This reagent yields intensely coloured derivatives with conjugated aldehydes. Enolic compounds may also react to yield less intensely coloured derivatives. Some sugars may be converted to the reactive aldehydes by oxidation with periodic acid. Extension of the procedure for the chromatographic visualization of some deoxy-ribosyl compounds is also described.

Metal ions in biological systems. II. The use of pM indicators in the presence of large molecules. A determination of the association constant of serum albumin.

J. Etti and S. M. Scoggan (Depart. of Biochem., Faculty of Medicine, Univ. of Ottawa, Canada) *Arch. Biochem. Biophys.* **91**, 27 (1960). The two wavelength pM spectrophotometric method previously introduced for the determination of metal ions, and shown to be valid in the presence of small molecules, has been extended to the case of media containing macromolecules such as proteins. The interaction of calcium with bovine serum albumin, using murexide as indicator, was chosen for investigation since it permitted a comparison of the binding constant thus derived with the values found in the literature and obtained by methods based on a wider variety of principles than for any other protein.

Photometric titration of weak acids in nonaqueous media. Determination of phenols in isopropyl alcohol.

L. E. I. Hummelstedt and David N. Hume (Depart. of Chem. and Lab. for Nuclear Sci., Massachusetts Inst. of Tech., Cambridge 39, Mass.) *Anal. Chem.* **32**, 1792 (1960). Photometric titrations of 16 weak acids, mainly phenols, were performed in com-

mercial isopropyl alcohol using tetra-n-butylammonium hydroxide in isopropyl alcohol as titrant. In favourable cases, upto four components in a mixture were resolved if a suitable change in wavelength setting was made during the titration. Nonlinear photometric titration curves for phenols provide new evidence for complex formation between phenols and phenolate ions.

A colorimetric qualitative test for glycine.

R. L. Sublett and J. P. Jewell (Tennessee Polytechnic Institute, Cookeville, Tenn.) *Anal. Chem.* **32**, 1841 (1960). A colour reaction between glycine, ethyl chloroformate, and pyridine was studied as a qualitative test for glycine. Results indicate that the reaction is specific for glycine, pyridine, and the alkyl chloroformates. This method can be adapted to spot testing for glycine with a sensitivity of 1 to 2 μ g. The coloured compound is stable in some polar solvents.

Effect of denaturation on the ultraviolet absorption spectra of proteins.

A. N. Glazer and Emil L. Smith, *J. Biol. Chem.* **235**, PC 43 (1960). The present communication deals with an extension of the investigation of the effect of denaturation on the ultraviolet absorption spectra of proteins in the wavelength range 200 to 320 m μ . The crystalline, salt free proteins investigated were, among others, insulin, ribonuclease, lysozyme, papain, chymotrypsinogen, pepsin, ovalbumin and bovine serum albumin. The treatments employed were acid and alkali denaturation with detergents, or a combination of two or more of these techniques. On comparing the native protein with the denatured one by difference ultraviolet spectroscopy, it was observed that in addition to the frequently reported difference peaks due to tyrosine and tryptophan side chains at 278 to 285 and 293 m μ , respectively denaturation was invariably associated with the appearance of a far more prominent peak at 230 to 235 m μ . On the basis of the observations made, it would appear likely that the change in the environment of the peptide backbone of proteins resulting from denaturation may contribute largely to the observed difference peak.

N. N. G.

Interpretation of the ultraviolet spectral changes of proteins.

Sam Yanari and F. A. Bovey, *J. Biol. Chem.* **235**, 2818 (1960). Ultraviolet spectral changes occurring when proteins are modified

structurally have been measured (chiefly by means of difference spectra) and compared to those occurring in the spectra of aromatic amino acids under parallel conditions and in the spectra of aromatic model compounds in solvents of varying polarity and polarizability. A difference spectrum is not a reliable measure of a solvent induced spectral shift because of the varying contributions of spectral broadening and all over increase in absorption in different solvents. The inductive effects of vicinal charges as such on aromatic amino acid spectra are too small to account for the changes occurring in protein spectra. The short wavelength shifts in the phenylalanyl, tryptophyl and tyrosyl absorption regions observed when proteins are modified structurally are closely paralleled by changes in the spectra of benzene, indole and phenol respectively, on passing from solvents of higher to those of lower refractive index. The long wavelength shifts of the spectra of phenol, tyrosine and their derivatives in urea and in sodium acetate are not caused by dipole-dipole and ion-dipole interactions, as suggested by others. These shifts are also related to the polarizability of the solvent. The possible occurrence of tyrosyl-carboxylate ion-dipole bonding in proteins is not excluded by these findings except in the case of pepsin, where it clearly cannot account for the magnitude of the changes in the tyrosyl absorption.

N. N. G.

Ultraviolet difference spectra and the internal structure of proteins.

S. J. Leach and Harold A. Scheraga, *J. Biol. Chem.* **235**, 2827 (1960). While a variety of solvent and ionic effects may give rise to shifts in the ultraviolet spectra of proteins, it is possible, by using auxiliary data (such as the pH dependence of reversible denaturation) to determine whether the effects are due in any part to side chain hydrogen bonding. Although the pH dependence of reversible denaturation can be explained in terms of a model involving hydrogen bonds, this does not preclude the possibility of accounting for the phenomenon in terms of a model based on hydrophobic bonding, including electrostatic effects. Although due caution is required in interpreting different spectra, and each protein must be evaluated on its own merits, data of this type are clearly useful in the location of internal interactions in proteins.

N. N. G.

Chromatographic analyses of the free amino-acids, organic acids and sugars in wheat plant extracts.

Byron S. Miller and T. Swain, *J. Sci. Food Agric.* **11**, 344 (1960). Plants of three hard red winter wheat varieties differing in their resistance to attack by hessian fly (*Mayetiola destructor* Say) were compared at the fourth leaf stage for their content of constituents extractable by 80% ethanol. Eleven amino-acids, five organic acids and two inorganic acids were identified. Seven sugars were separated, two of which were unidentified polysaccharides. The main difference was that the susceptible variety (Tenmarq) contained allulose, or allulose in combination with some other component. This compound was present to a lesser extent in the semi-resistant variety (Ponca) and not present in the plants of the resistant variety (C. I. 12855). Sorbitol also was found in Tenmarq but not in the other varieties.

Determination of the components of plant cuticles.

J. T. Martin, *J. Sci. Food Agric.* **11**, 635 (1960). Quantitative methods are described for the determination of waxy substances and cutin in plant cuticles. Surface waxy materials are obtained by immersing leaves or fruits in chloroform at room temperature; waxy substances embedded within the cuticles of fruits are recovered by further extraction of the skin after surface washing. Acidic materials are removed from the extract, and true wax and 'oil' fractions are obtained by partition between n-heptane and methanol. The cuticular membranes are then separated by treatment with ammonium oxalate-oxalic acid solution, and the cutin in the membranes is determined by saponification. Work by other investigators on the nature and determination of components of plant cuticles is reviewed.

Analysis by electron microscopy and infectivity of foot-and-mouth disease virus in moving-boundary and zone ultracentrifugation.

S. S. Breese, Jr., R. Trautman and H. L. Bachrach (U.S. Depart. of Agric., Agricul. Res. Service, Animal Disease and Parasite Res. Divn., Plum Island Animal Disease Lab., Greenport, Long Island, New York) *Arch. Biochem. Biophys.* **87**, 1 (1960). Several techniques were used in the study of ultracentrifugal separation of foot-and-mouth disease virus, type A, from partially purified suspensions. A moving-boundary preparative ultracentrifuge method was used to confirm the sedimentation rate of 140 S. Zone centrifugation of the virus was done in a D₂O and ammonium

acetate medium. Direct analysis by infectivity and virus particle counts of the various fractions was effective in determining the optimum region for virus recovery. The number of droplets required to determine reliable virus concentration was reduced by the chi-square statistical analysis of particle counts.

Gelation phenomena in degraded fibrinogen and fibrin.

M. Derechin and Sara Szuchet (The Lab. of Chem., Dental School, Univ. of Chile and the Instituto Nacional de Microbiologia, Buenos Aires, Argentina) *Arch. Biochem. Biophys.* **87**, 100 (1960). Fibrin lysed by plasmin was made to gel again by the action of many different reagents. Lysed fibrinogen could also be made to clot by the same reagents provided that thrombin was first added. The ability of the reagents which produce this clotting effect was studied quantitatively.

The identification, by chromatography, of plant phenolic acids.

R. K. Ibrahim and G. H. N. Towers (Botany Depart., McGill Univ., Montreal, Canada) *Arch. Biochem. Biophys.* **87**, 125 (1960). A method is described for the separation and identification by two-directional paper chromatography of 21 phenolic acids, many of which are known to occur in various species of higher plants. A very brief survey of species indicates that the distribution of some of these compounds is much more extensive than has been supposed.

THEORIES

Hydroxypyruvic acid formation in *Aspergillus niger*.

Francis J. Behal (Depart. of Biochem., Medical College of Georgia, Augusta, Georgia) *Arch. Biochem. Biophys.* **88**, 110 (1960). The ability of the mold, *Aspergillus niger*, to convert 3-phosphoglyceric acid to hydroxypyruvic acid has been demonstrated. Hydroxypyruvic acid has also been shown to counteract the inhibitory effect on growth elicited by iodoacetic acid. Possible relationships between hydroxypyruvic acid formation and growth are discussed.

Chromatographic studies on trypsin, trypsinogen and the activation process.

Irvin E. Liener (Depart. of Agricul. Biochem., Univ. of Minnesota, St. Paul, Minnesota) *Arch. Biochem. Biophys.* **88**, 216

(1960). Crystalline preparations of trypsin and trypsinogen were chromatographed on carboxymethylcellulose at pH 3.2 using gradient elution of increasing salt concentration. Crystalline trypsin contained an inert component which could be quantitatively precipitated with 0.05M CaCl_2 at pH 8. This permitted the recovery of trypsin which was chromatographically homogeneous. A chromatographic study of the autocatalytic activation of trypsinogen in the presence and absence of calcium ions suggested that this inert protein may be the result of activation in the absence of calcium ions. It was also demonstrated that this chromatographic technique could be applied to the large-scale preparation of trypsinogen which is relatively low in trypsin.

The acid-soluble collagen of cod skin.

E. Gordon Young and J. W. Lorimer (Atlantic Reg. Lab., National Res. Council of Canada, Halifax, Nova Scotia, Canada) *Arch. Biochem. Biophys.* 88, 373 (1960). Cod skin has been found to contain 75% collagen, 10% other protein, 2.5% peptides and free amino acids, 0.6% mucopolysaccharide, 1.0% lipid, and 12% ash. About 95% of the total solids were dissolved by repeated extraction of the skin with mild aqueous solvents of pH 3.4-8.7 at 3-90°C. Collagen has been extracted with buffers of various organic hydroxy acids and their sodium salts at pH 3.6. It was recovered as needle-like fibrils, about $30 \times 1\mu$, with characteristic banding. It contained 18.2% N, 0.02% hexosamine, 8.0% hydroxyproline ($\approx 4.7\%$ of the total N) and a distribution of 18 amino acids quantitatively identical with collagen from cod swim bladder. The specific optical rotation changed from $[\alpha]_D^{50} - 349 \pm 50^\circ$ to $[\alpha]_D^{23} - 107 \pm 2^\circ$ and was partially reversible with time and temperature to $[\alpha]_D^{50} - 223 \pm 12^\circ$. The value for S_{20w}° was 3.17 ± 0.10 S, measured at 6.9°C., and for (η) 12.8 ± 0.3 dl./g. measured at 1.4°C. From these values the particle weight was calculated to be $28,000 \pm 20,000$ for an elongated rod of 12.1 A. diameter and 2810 A. length on the assumption of $\bar{v} = 0.700$. An irreversible change into two components occurred sharply at $13 \pm 0.5^\circ\text{C}$, as shown especially clearly in the ultracentrifuge. The value for (η) of the mixture was ~ 1 .

Protein synthesis from amino acids associated with ribonucleic acid.

George C. Webster (Depart. of Agricul. Biochem., The Ohio State Univ., Columbus, Ohio) *Arch. Biochem. Biophys.* 89, 53

(1960). The polynucleotide (sRNA) which reacts with amino acids in the presence of amino acid-activating enzymes and adenosine triphosphate has been purified considerably by ethanol fractionation. Maximal transfer of amino acids from this purified sRNA to the protein of isolated ribonucleoprotein particles requires rather sharply defined optimal conditions. Under such conditions, however, the amino acids bound to sRNA are converted into "soluble" protein more efficiently than are free amino acids.

Collagen solubilization by mammalian proteinases.

Norman H. Grant and Harvey E. Alburn (Biochem. Depart., The Wyeth Inst. for Medical Res., Radnor, Pennsylvania) *Arch. Biochem. Biophys.* 89, 262 (1960). Collagen is sometimes rapidly metabolized *in vivo*, but clear evidence of proteolysis by tissue enzymes has been lacking. In this study, the solubilization and proteolysis of washed, dissected collagen fibres from rat tail tendons were examined at 38° and pH 7.4 under the influence of chemicals to which collagen may be exposed *in vivo*. Trypsin, chymotrypsin, elastase, and the endopeptidase from procaryo-peptidase all solubilized collagen in the presence of calcium salts or salicylates. Arginine, creatinine, and guanidine enhanced this solubilization and lowered the calcium and salicylate levels required. The adsorptive capacity of some collagens, particularly for calcium, suggests that adequate concentrations of sensitizing agents could occur locally *in vivo*.

The role of the carbohydrate moiety in the structure of the collagen fibril.

Irving Oneson and John Zacharias (Depart. of Biochem., Ethicon, Inc., Somerville, New Jersey) *Arch. Biochem. Biophys.* 89, 271 (1960). Collagen isolated from different tendons of the steer was found to contain a firmly bound polysaccharide in amounts ranging from 0.29 to 0.85% depending on the location of the tendon. Viscosities of dilute acetic acid dispersions of the collagen varied in an inverse manner with the amount of bound polysaccharide. Collagen with a polysaccharide content of over 1% was no longer dispersible. Treatment of the collagen dispersions with dilute ficin extracts resulted in an increase in the viscosity followed by a decrease in the viscosity of the dispersion. These results are discussed with regard to the structure of the collagen fibril.

The relative ionizations of the mercapto and amino groups in cysteine.

George Gorin and C. W. Clary (Depart. of Chem., Oklahoma State Univ., Stillwater, Oklahoma) *Arch. Biochem. Biophys.* **90**, 40 (1960). Cysteine ionizes to give the ions $\text{—SCH}_2\text{CH}(\text{NH}_3^+)\text{COO}^-$ and $\text{HSCH}_2\text{CH}(\text{NH}_2)\text{COO}^-$. The relative amount of the former is greatly diminished by adding ethanol but is little affected by changes in ionic strength; this is indicated by changes in the ultraviolet absorption. Calculations based on absorption measurements indicate that the ratio of the concentrations of these ions in water cannot be lower than about 1.8, but an upper limit cannot be set with certainty. These results are consistent with the value of 2 determined by other means.

Amino acid turnover and protein synthesis in leaves.

David Racusen and Murray Foote (Depart. of Agricul. Biochem., The Univ. of Vermont, Burlington, Vermont) *Arch. Biochem. Biophys.* **90**, 90 (1960). Detached bean leaves were allowed to fix C^{14}O_2 in the light for 10 minutes, and the remaining C^{14}O_2 was flushed from the system. Subsequent changes in amino acid and protein radioactivity were used to calculate amino acid turnover rates and the rates of protein synthesis from particular amino acids. The free amino acids serine, glycine, threonine, alanine and the leucines had roughly the same total turnover times (about 15-20 min.), whereas free aspartic acid turned over once in about 50 minutes. Protein synthesis occurred at a rate roughly equal to a 2% increase per hour.

On the mechanism of enzyme action. LXX. Urea denaturation of trypsin and acyltrypsins.

J. F. Riordan, M. Bier and F. F. Nord (The Lab. of Organic Chem. and Enzymology, Fordham Univ., New York) *Arch. Biochem. Biophys.* **90**, 125 (1960). Trypsin and its acetyl and succinyl derivatives were exposed to urea solutions of various concentrations. The resulting changes, as measured by activity and sedimentation studies are due to denaturation, both reversible and irreversible, and to self-digestion. The effect of acylation on these processes is discussed and, in addition, the sequence of steps leading to the final inactive product considered. The action of urea is compared to that of heating the enzymes, and the similarities are indicated.

On the mechanism of enzyme action. LXXI. Acylations of trypsin in organic solvents.

S. M. Vratsanos (Lab. of Organic Chem. and Enzymology, Fordham Univ., New York) *Arch. Biochem. Biophys.* **90**, 132 (1960). Acetylation of trypsin in dimethyl sulfoxide solutions is a reaction highly specific for the free amino groups of the enzyme. The progressing acetylation causes a gradual reduction of the activity characterized by a complete inactivation upon the introduction of about 15 acetyl groups per trypsin molecule. By increasing the bulk of the substituent acyl group this number is reduced. The inactivation caused by the substitution is apparently associated with a specific configuration that the enzyme assumes in the organic solvent. In formamide, the introduction of acetic anhydride results in formylation rather than acetylation. The observation of inactivation in the presence of trypsin competitors for the utilization of the reagent offers a sensitive means of evaluation of the reactivities of various functional groups of proteins.

The effect of growth on the composition of avian muscle.

J. W. T. Dickerson (Medical Research Council Department of Experimental Medicine, University of Cambridge) *Biochem. J.* **75**, 33 (1960). Pectoral muscle from Rhode-Island Red cockerels at 0, 2½, 4 and 27 weeks of age were analysed for water, chloride, sodium, potassium, phosphorus and magnesium, and the total nitrogen was divided into non-protein, sarcoplasmic-, fibrillar- and extracellular-protein nitrogen.

The amounts of water, chloride, sodium and extracellular-protein nitrogen/kg. decreased and those of potassium, phosphorus and magnesium increased during the first 2½ weeks. Potassium and phosphorus fell from this age to a lower level in the adult. The fibrillar proteins increased mainly during the first 2½ weeks whereas the main increase in the sarcoplasmic proteins was between 2½ and 4 weeks. At 4 weeks the muscle had an almost adult composition.

Calculations showed that the increase in the proportion of the cellular phase was accompanied by an increase in the amount of protein nitrogen/l. of cell water, whereas the amount of sodium plus potassium/l. of cell water decreased.

The possible influence on cell composition of the uneven distribution of cellular constituents is briefly discussed.

Studies in Flavinogenesis. 6. The role of threonine in riboflavin biosynthesis in *Eremothecium ashbyii*.

T. W. Goodwin and A. A. Horton (Department of Biochemistry, The University, Liverpool 3) *Biochem. J.* 75, 53 (1960). *Eremothecium ashbyii* incorporates generally-labelled L- (^{14}C) threonine into riboflavin to the extent of 4%. C-1 and C-2 of threonine are incorporated as glycine into C-4a+C-9a of riboflavin. C-3 and C-4 of threonine are not incorporated into riboflavin. The enzyme threonine aldolase, splitting threonine into glycine (C-1+C-2) and acetaldehyde (C-3+C-4), is present in *E. ashbyii*.

The interconversion of glutamic acid and aspartic acid in respiring tissues.

H. A. Krebs and D. Bellamy (Medical Research Council Unit for Research in Cell Metabolism, Department of Biochemistry, University of Oxford) *Biochem. J.* 75, 523 (1960). Homogenates of rat and pigeon liver, pigeon-breast muscle and sheep-kidney cortex convert added glutamate into aspartate. Under some conditions, the amounts of glutamate removed and aspartate formed are approximately equal. The homogenates also convert aspartate into glutamate, the amounts of glutamate formed being of the order of 50% of the amounts of aspartate removed. In many cases, reactions (1) and (2) account for most of the oxygen consumption in the presence of glutamate or aspartate. An almost stoichiometric conversion of glutamate into aspartate also occurs in rat-brain mitochondria. In mitochondria of rat and pigeon liver and of pigeon-breast muscle, the yield of aspartate was only 20-30% of the glutamate removed. Washed suspension of *Escherichia coli* and *Alcaligenes faecalis* did not accumulate aspartate on addition of glutamate.

The formation of fibrils from collagen solution. 1. The effect of experimental conditions: Kinetic and electron-microscope studies.

C. G. Wood and M. K. Keech (Department of Medicine, University of Leeds) *Biochem. J.* 75, 588 (1960). The precipitation of collagen fibrils in solutions of acid-soluble collagen extracted from calf dermis has been followed turbidimetrically under a range of experimental conditions and the final precipitates have been examined by electron microscopy. All the precipitates consisted of fibrils bearing 640 Å striations and in each precipitate the distribution of fibril width was fairly narrow. Lateral aggregation of

the fibrils was most pronounced in those precipitates containing the widest fibrils. When the rate of precipitation was increased by increasing the temperature or lowering the ionic strength, fibril width decreased, but when the rate was increased by reducing the pH, fibril width increased. The variation of rate of precipitation with ionic strength and pH indicates that it is controlled to a significant degree by electrostatic interaction between the soluble collagen particles. All precipitation curves showed a lag period, followed by a sigmoid growth curve. Both phases were accelerated by increase of temperature but the width of the ultimate fibrils was affected only if the temperature was increased during the lag period. It is concluded that most of the fibrils were formed during the lag period. These observations are discussed in relation to the development of collagen fibrils *in vivo*.

The formation of fibrils from collagen solutions. 2. A mechanism of collagen-fibril formation.

G. C. Wood (Nuffield Gerontological Research Unit, Department of Medicine, University of Leeds) *Biochem. J.* 75, 598 (1960). Fibril formation is regarded as the result of two processes: (a) nucleation, i.e., the aggregation of soluble collagen particles to form nuclei, the smallest aggregates capable of existing as a separate phase; (b) growth of the nuclei into fibrils by accretion of further soluble collagen particles. It is assumed that reaction of the soluble collagen particles with the surface of the growing fibrils controls the rate of growth and that the former process is proportional to the surface area of the precipitate and to the collagen concentration. Equations are derived which qualitatively account for the occurrence of a lag period in precipitation, where the nucleation process predominates over growth, and for the observation that the final distribution of fibril width is determined during the lag period. The equation for growth gives a precise description of the shape of precipitation curves over a wide range of conditions. Predictions about fibril width are consistent with experimental observations. The activation energy for growth is calculated to be 27 kcal./mole (at pH 7.1, I 0.23, collagen concentration 0.05%).

The formation of fibrils from collagen solution. 3. Effect of chondroitin sulphate and some other naturally occurring polyanions on the rate of formation.

G. C. Wood (Nuffield Gerontological Research Unit, Department of Medicine, University of Leeds) *Biochem. J.* 75, 605 (1960).

Low concentrations of heparin and deoxyribonucleic acid have been found to retard fibril formation in solutions of acid-soluble collagen at pH 7, I 0.23 and 25°. Two types of chondroitin sulphate (A and C) and a preparation rich in keratosulphate accelerated fibril formation. Another type of chondroitin sulphate (B) and hyaluronic acid had no effect. Those polyanions which accelerated precipitation reduced fibril width and those which retarded precipitation increased it. The accelerating effect of chondroitin sulphate A increased with decreasing pH in the range pH 6.8 and with increasing I in the range 0.13-0.31. Chondroitin sulphate A accelerated precipitation only when present during the lag period. This observation supports the conclusion from earlier work that collagen fibrils form as the result of two consecutive processes, nucleation and growth, and it is concluded that chondroitin sulphate A accelerates precipitation by affecting nucleation. Only a very small proportion of the added chondroitin sulphate was incorporated into the collagen precipitate. When collagen solutions were pretreated with phosphate buffer, pH 7, at 0° addition of chondroitin sulphate A retarded subsequent precipitation at 25°, indicating that nucleation had taken place during pretreatment and that the observed retardation was due to the effect of chondroitin sulphate A on growth. The mode of action of the polyanions is considered in the light of the two-step mechanism of fibril formation and the findings are discussed in relation to the possible role of mucopolysaccharides in the formation of collagen fibrils *in vivo*.

The ultraviolet fluorescence of proteins in neutral solution.

F. W. J. Teale (Department of Biochemistry, The University, Sheffield 10) *Biochem. J.* 76, 381 (1960). The fluorescence spectra, fluorescence-excitation spectra and absolute quantum yields of 21 globular proteins have been measured in neutral solutions. Phenylalanine fluorescence was not observed in the presence of other aromatic groups, and tyrosine fluorescence was detected in low yield with band maximum at 304 m μ only in the absence of tryptophan. In proteins containing tryptophan the fluorescence spectrum of this residue alone is observed, irrespective of the wavelength of the exciting light, even in those cases where tyrosine predominates in absorption. The band maxima vary in wavelength between 328 and 342 m μ , and the overall quantum yields 3.8-15.2% in water. Detailed examination of the change in tryptophan quantum yield in the excitation region between 280 and 310 m μ reveals

that energy transfer from tyrosine to tryptophan does not take place to any appreciable extent. The similarity of all protein-excitation spectra with that of either tyrosine or tryptophan shows that light absorbed by cystine or the peptide bond does not contribute to protein fluorescence. Modification of the protein structure by 8 M-urea produces large and in some cases reversible changes in tryptophan fluorescence, leading to similar yields and fluorescence spectra in most of the proteins examined. The slight structural change involved in the activation of chymotrypsinogen increases the quantum yield by 32%. Propane-1:2-diol increased the yield of all the proteins except the serum albumins and lysozyme. The absence of tyrosine fluorescence in many proteins is explained by the quenching action of the tyrosyl-carboxylate hydrogen bond, and is correlated with the pK values for the phenolic ionization. The role of this linkage in the maintenance of the protein tertiary structure is briefly discussed.

Some properties of neutral-salt-soluble collagen. 1.

J. H. Fessler (Department of Biochemistry, University of Oxford) *Biochem. J.* 76, 452 (1960). Neutral-salt-soluble collagen was extracted from the skins of young rabbits and rats and purified by repeated salting-out. The purification process was studied. This neutral-salt-soluble collagen was separated into three parts: (a) fraction A, which reversibly formed fibres at 37°, the fibres dissolving again on cooling, (b) fraction B, which did not form fibres on warming to 37°, and (c) fraction C, which on warming to 37° formed fibres that did not dissolve on subsequent cooling. The proportions of these fractions were found to be independent of concentration and pH over a limited range. Evidence for the existence of three fractions was obtained from a study of the effects of repeated warming and cooling. The original material and the separated fractions were investigated by sedimentation, viscosity and streaming birefringence analyses. No significant differences were found between the fractions. A representative particle was estimated as a highly elongated rod, several thousand Angstrom units long, with a particle weight of about 500 000. No differences in the hydroxyproline, proline or glycine contents of the separate fractions were found. Hexose and hexosamine contents were negligible. Neutral-salt-soluble collagen, was found to contain not more than one atom of phosphorus in a particle of 340 000 molecular-weight units. The phosphorus is probably present as an impurity.

Some properties of neutral-salt-soluble collagen. 2.

J. H. Fessler (Depart. of Biochem., Univ. of Oxford, and Depart. of Med., Harvard Medical School and the Massachusetts General Hospital, Boston, U.S.A.) *Biochem. J.* **76**, 463 (1960). Fibres formed from concentrated solutions of fraction B of neutral-salt-soluble collagen by salting-out had the typical striated appearance of collagen fibres in the electron microscope. No fibres were formed on warming enriched solutions of fraction B in 0.067 M-phosphate buffer, pH 7.4, although the collagen concentration was several times as great as concentrations at which fraction A forms fibres under these conditions. Solubility properties of fraction A varied considerably with temperature in the range 27-37°, and were not those of a single Phase-Rule component. At pH 3.7 the specific optical rotation of fraction B varied with temperature (0-37°), whereas those of fractions A and C did not. The polarimetric behaviour of solutions of neutral and acid-soluble collagen were identical on varying the temperature at pH 3.7. Conversion into gelatin was rapid at 39.5°. The glycine of fractions A, B and C had identical specific radioactivities in samples isolated from guinea pigs 6 hr. after injection of (¹⁴C) glycine. The rate of precipitation of neutral-salt-soluble collagen varied directly with hydrogen-ion concentration in the range pH 6.5-7.4. The activation energy was about 80 kcal./mole/degree at pH 6.8. The temperature-dependent-solubility behaviour of neutral-salt-soluble collagen and the nature of fractions A, B and C are discussed.

Study of a proteolytic enzyme from rabbit spleen.

C. Lapresle and T. Webb (Service de Chimie microbienne, Institut Pasteur, Paris) *Biochem. J.* **76**, 538 (1960). The proteolytic activity of rabbit-spleen extracts towards human serum albumin has been studied. With serum albumin as substrate a method of measuring the proteolytic activity of spleen extracts has been developed, based on the determination with the biuret reagent of the amount of products which are not precipitable by trichloroacetic acid. The enzyme responsible for this proteolytic activity has been purified by adsorption of inactive material on diethylaminomethylcellulose and carboxymethylcellulose. Chromatography on diethylamino-ethylcellulose has demonstrated the existence of only one enzyme in the purified preparation. The optimum pH and the Michaelis constant of this enzyme are the same as those

of the proteolytic activity in the crude preparation. It was therefore concluded that this enzyme is responsible for the proteolytic activity of the crude spleen extracts. A comparative study of the immunoelectrophoresis patterns given by human-serum albumin, degraded with the crude and purified spleen extracts, has shown that it is this enzyme which is responsible in both cases for the splitting of the antigenic structure of human-serum albumin.

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NOTES AND NEWS

Cellulose Precursor Found

Biosynthesis of cellulose is becoming better understood as intermediates in the process are isolated. The precursor of cellulose seems to be clearly defined as a complex molecule made up roughly of 10% glucose and 9% lipid, according to Dr. J. Ross Colvin of the National Research Council, Ottawa, Canada. The exact chemical make-up of the lipid remains unknown, however.

Work at NRC shows that biosynthesis of cellulose starts when *Acetobacter xylinum*—one of two bacteria known to make cellulose extracellularly—forms a glucose-lipid molecule. Its molecular weight runs about 2000. From inside the bacteria, the molecule passes through the cell wall because of its high lipid fraction. An enzyme accompanies the molecule, Dr. Colvin told Division of Cellulose Chemistry's luncheon.

After passing into a buffered medium containing the bacteria and glucose, the enzyme splits the lipid-glucose molecule. The glucose is attached to the end of a cellulose microfibril, while the lipid recycles to the bacteria. The enzyme causing the reaction has not been isolated nor named.

Chemical and Engineering News: April 18, 1960.

Amino acids can copolymerize below 100° to give polymers very similar to natural proteins

Studies of thermal copolymerization of amino acids have recently advanced our understanding of the origin of life. Kaoru Harada and Dr. Sidney W. Fox of Florida State University's chemistry department and Oceanographic Institute have found that amino acids can copolymerize with polyphosphoric acid between 70° and 100°C to give 10 to 20% yields of proteinoids after 100 hours of heating.

These proteinoids are like natural proteins in all respects studied but one. The products are not antigenic; that is, they don't generate antibodies when introduced into animals, Mr. Harada told the Division of Biological Chemistry.

If the proteinoids are dissolved in hot water and the water then cooled, millions of microscopic spheres result. These have many properties of bacterial membranes. They are the same size (1 to 3 microns in diameter) and shape as cocci, believed by some to be the most primitive bacteria.

In studying the proteinoids over a two year period, Mr. Harada, Dr. Fox, and others have found that the polymers contain all of the 18 common amino acids, with mean molecular weights of polymers so far prepared, going as high as 9000. Carbon analysis of the proteinoids has been found to be 51.0 hydrogen 4.79, and nitrogen 13.2.

Polymer compositions are altered by changes in the composition of reactants, temperature, heating time, and other factors. Sometimes, the scientists find that the composition looks like that of natural proteins. Ordering in the polymerization is suggested by differences between N-terminal composition and total composition. It has also been found that racemization occurs during the polymerization, though some bacterial proteins are said to include substantial amounts of D-amino acids. Infra-red absorption patterns show linear peptide bonds.

Proteinoids solubilities, according to Mr. Harada, resemble those of globulins, with a small amount of albumin. They are completely soluble in many dilute salt solutions and can be salted out of solution, he says. Other polymer properties: conformation to standard colour tests for proteins (Hopkins-Cole, xanthoproteic); electrophoretic mobility; and susceptibility to attack by proteolytic enzymes.

Chemical and Engineering News: April 18, 1960.

DNA Helix taken apart put together again

A giant step toward better understanding of the chemistry of deoxyribonucleic acid—the blueprint of heredity—has resulted from research at Harvard University. In a report to the National Academy of Sciences, meeting in Washington, D.C., Dr. Paul M. Doty described techniques which allow scientists to put together DNA molecules that never existed before and to incorporate them into living cells. Thus, they can learn more about how hereditary traits are carried in DNA and how they are passed on when cells divide.

Using the new method, the Harvard group—Dr. Doty, Dr. Julius Marmur, Joseph Eigner, Dorothy Lane, and Carl Schildkraut—have already been able:

To split the double helix of the DNA molecule into its two strands and put it back together again without destroying its biological properties.

To build “hybrid” DNA’s, using strands from two different strains of bacteria. These hybrids work in the bacterial cell just as well as natural DNA.

To make hybrids of DNA from two different bacterial species. But they have not yet incorporated such a hybrid into living cells. To show that a gene—which is just a small part of a DNA strand—is still active, even if it is only on one of the two chains.

“Unzipped”:—Dr. Marmur and Miss Lane find that a DNA helix can be “unzipped” by denaturing it at 100°C., yielding two disorganized, highly flexible strands. When they cool the solution slowly, the strands recombine to form a helix of “renatured” DNA. If they cool the denatured material quickly, the chains fail to recombine.

The divided DNA strands are not damaged by fast cooling. When they are reheated and cooled slowly, they revert to the two-stranded, active form.

To determine the amount of recombination that takes place during the process, Dr. Marmur uses DNA from different strains of *Diplococcus pneumoniae*—one resistant to streptomycin and the other a “wild” strain showing no such resistance. When the mixture of DNA’s is denatured, the two strands of each helix separate. But when the DNA helixes reform on cooling, a “marked” strand—carrying streptomycin resistance—can combine with a wild strand, which doesn’t carry the marker. Thus, a hybrid DNA molecule results.

A culture of wild *D. pneumoniae* incorporates the hybrid and develops a resistance to streptomycin. By measuring the amount of transformation that takes place, Dr. Marmur estimates that up to 40% of the original DNA molecules recombine into biologically active renatured DNA. Similar results have been obtained with *D. pneumoniae* carrying different markers—resistance to erythromycin or bryamycin.

Chemical and Engineering News: May 9, 1960.

Enzymatic Fungicides show promise

A new research approach at the University of Maine—enzyme systems to fight fungus diseases of food crops—is gaining importance in the light of the Government’s tough policy against toxic residues on foodstuffs. Enzymes have two strong points in their favour in the battle: no toxic residue, no harmful (phytotoxic) effect on the crop.

The Maine Research team finds that the polysaccharide enzyme, chitinase, specifically attacks the chitin in the fungal cell wall, apparently without harming the plant. And, being specific for chitin, the enzyme has no effect on humans. It quickly hydrolyses the chitin and ruptures the cell wall, thus killing the extruding protoplast naturally by exposure to air. A solution containing as little as 0.1 p.p.m. of chitinase completely inhibits spore germination of *Aspergillus niger*, the common black mold found on many food products. Moreover, its effectiveness is not limited to this one fungal organism, they report. It should work on any fungal cell protected by chitin.

Lots of possibilities:—The enzymatic fungicide approach appears more far-reaching than simply the chitin-chitinase system. It might be extended to include enzymes which specifically attack other materials known to be present in fungal cell walls. Enzymes such as cellulase, the proteases, and the lipases are likely looking candidates for future development, Mr. Hilborn believes.

And the use of enzymes may not be confined to plant disease control. Mrs. Farr and Mr. Hilborn suggest the possibility that such an enzymatic approach might be used to treat skin diseases of fungal origin in man and higher animals. Preliminary results with the chitinase extract on three fungus species that cause human skin diseases—*Epidermophyton floccosum*, *Microsporum gypseum*, and *Tricophyton gallinae*—point to the possibility, but their cell chemistry has not yet been resolved, Mrs. Farr tells C & EN. Insect pest control, too, shapes up as another attractive area for the new approach. A number of chemical and pharmaceutical companies reportedly have launched research programmes in enzymatic fungicides.

Chemical and Engineering News: May 30, 1960.

Shipments during January 1961

2,097 bales tanned cow hides, 149 bales tanned cow calf skins, 22 bales tanned buffalo hides, 196 bales tanned buffalo calf skins,

330 bales tanned goat skins, 354 bales tanned sheep skins to U. K., 123 bales tanned cow calf skins, 59 bales tanned buffalo calf skins, 694 bales tanned goat skins, 347 bales tanned sheep skins to Continent; 88 bales tanned buffalo hides, 95 bales tanned buffalo calf skins, 261 bales tanned goat skins, 10 bales tanned sheep skins to U. S. A., 11 bales tanned goat skins, 233 bales tanned sheep skins to Japan; 5 bales tanned buffalo calf skins, 12 bales tanned goat skins, 11 bales tanned sheep skins, 14 bales tanned cow hides to Australia & New Zealand to Aden. Total 5,111 bales.

The Mail: February 5, 1961.

Indian hides and skins

Free import by Italy urged

A plea for free import of tanned hides and skins into Italy was made by Mr. A. Nagappa Chettiar, at a dinner given by him to the members of the Italian Economic Mission.

Mr. Nagappa Chettiar said that after representations by the Indian trade delegation to Italy in 1959, the Italian Government had reduced the import duty on tanned hides and skins from 13 to 5 per cent from January 1960. He suggested that even this five per cent duty might be removed.

Senator Emillo Battista, leader of the mission, assured Mr. Chettiar and other trade interests in India of Italian collaboration for the development of trade between the two countries.

Mr. Battista, earlier, told the Tamil Chamber of Commerce that Italy had already passed legislation for the extension of credit facilities to other countries. Mr. Angelo Abellonio, a member of the mission, said they were interested in buying raw materials from India for the manufacture of leather goods.

The Mail: February 12, 1961.

Bone "Banks"

Success of German experiments

In modern medicine, the idea of medical "banks" or "exchange systems" has gathered ever more ground. Initially there were only "blood banks" which by means of stocks of each blood group were accumulated to be used for blood transfusion in

emergencies. However, recently attempts were also made to transplant entire organs. But the road from successful animal experiments to daily application in human medicine is a hard and arduous one. Attempts to make transplantations from one man to another show that there is a "biological barrier", due to the fact that the organism of a human being with its individual chemical structure of hormones, blood fluids and cells fights against the entry of any foreign substance. Thus skin parts transplanted will die, unless they come from the patient's own body. This behaviour of the human organism is due to the medical individuation of man, which has previously prevented the practical use of transplantation of organs. It is against this background that the new procedure for the transplantation of bones from calves or cows to men attains great significance. It was developed in the surgical clinics of the North German University of Kiel. Clinic tests have been very successful so far. Ever since its creation, the central laboratory has been called the "bone bank".

In the life of tissues and body fluids, the protein bodies and "haptenes" (carbon hydrates and fatty substances) form a close compound to create molecular groups. Whenever they are injected into another body, they produce what are called "anti-bodies", which struggle against the haptenes and prevent a sound growth of the transplanted foreign tissue. The extent of the "hostile" double potency grows with the size of the cell and vessel richness and increases tremendously in the case of vital organs. On the other hand, in the ideal case of the cell-poor, non-vessel tissue of the cornea of the human eye, the transplantation of substitute substances from people who have just died, has been able to save the power of vision for innumerable people. Of a similar good quality of little "anti-potency" however, are also bones and gristle and cartilage which are very poor in cell substances.

Ampoules for ever-ready use

The Kiel medical researchers at first freed the animal bone tissue to be transplanted from the protein, in order to avoid any future "anti-effects". The tissue must be sterile, however, must retain its form and structure. The bones of young calves were selected and cleaned of all sinew and tendon, fibre, periosteum and blood, cut into the bone splits as usual in bone surgery, and for three days were put into a 20 per cent hydrogen peroxide solution at 34°C. After drying for one day and 24 hours of sterilization in ether vapour, which at the same time also defatted the

tissue, the bone splits were finally ready and put into ampoules for ever ready use. They are cell-free and without vessels, very poor in protein and fats, and, for these reasons, can serve for the regeneration process in the hurt human bone tissue as guiding and supporting tissue. It grows germination tissue very speedily, without any destructive reaction. The foreign tissue, on the other hand, will also add to the healing process its own organical growth substances. Hundreds of operations by this method have been made with great success. The material can be obtained from calves and cattle, so that there is no scarcity of material. The product is almost equal to the material of the own body of the patient, which is hardly ever available. As the bone parts obtained in this manner can practically be conserved without limitation, the "bone bank" at Kiel can be held to have perfectly solved a great problem of medicine.

The Hindu: February 13, 1961.

Export to U.K. in January 1961

The following are the figures (in bales) of exports to the U.K. during January: cow hides 2,097; cow calf 149; buff hides 22; buff calf 196; goat skins 330 and sheep skins 354.

The Hindu: February 13, 1961.

The leather industry

Mr. R. Venkataraman, Minister for Industries, Madras, said in the Legislative Assembly that there was no slump in the leather industry in 1960, although there had been marked fluctuations in prices.

In reply to a question by Mr. A. A. Rasheed and Mr. V. K. Kothandaraman, the Minister said peak prices were last reached during January-February 1960. This was followed by a temporary fall in the demand from foreign countries, resulting in a decline of about 15 to 25 per cent from the peak prices. Of late, however, the demand for our leather from abroad had been rising, though very slowly. "There cannot, therefore, be said to be a slump in the leather industry," he added.

Answering supplementaries, the Minister said the present practice of having the auction in London fetched good prices for leather and they could not, therefore, change the procedure.

In reply to another question, Mr. Venkataraman said the Government proposed to establish an industrial estate exclusively for leather goods and footwear at Perambur at an estimated cost of Rs. 11,54,200 (non-recurring) and Rs. 30,730 (recurring). The intention was to commence work in 1961-62, he said.

The Hindu: February 23, 1961.

Cattle disease control

Vaccine production at Ranipet

Production of potent sera and vaccines for the control of most of the common diseases of livestock is going on apace in the Research Institute at Ranipet, so that it has been able not only to provide the sera and vaccines for the requirements of the State, but also to offer to other neighbouring States, like Mysore, Andhra and Kerala. Freeze-dried Rinderpest, Ranikhet and Fowl-pox vaccines are now being released from the Institute for the first time. This Institute has now been developed into a pucca Research Centre on modern lines with the latest equipment to improve the efficiency and keeping the quality of the biologicals and to ultimately reduce the cost of production.

Because of timely vaccination of cows and buffaloes during actual outbreak of diseases and also in free areas, the disease position is said to have improved considerably, protecting several thousands of valuable cattle and saving lakhs of rupees to the agriculturists.

This Research Institute is said to be the first of its kind in the country, having equipment and modern devices for the production of and research in animal biologicals. In addition to the production of biologicals, research work in connection with the improvement of the biological products and study of the different organisms, found responsible for causing the disease under field conditions, and manufacture of new drugs to control contagious and infectious diseases of livestock are undertaken here.

The Hindu: February 24, 1961.

Cattle wealth of India

Need to develop

Inaugurating the fourth Madras State cattle show and fifth poultry show at the Congress Exhibition grounds, Teynampet, Mr. K. Kamaraj, Chief Minister of Madras, said that it was vital

that cattle population in our country should be protected because India was essentially an agricultural country. While machines had been a great help in the development of agriculture in our country, the important role played by the cattle could not be ignored and the two can never be separated. If the cattle population is allowed to be depleted then the children would be handicapped for want of milk. It was also necessary to see that there was an increase in milk production and make it available to the people at cheap rates, the Chief Minister said.

Mr. M. Bhaktavatsalam, Minister for Agriculture, who presided, said that the cattle shows were becoming popular and the Government were hoping to hold the next show at Tiruchi and thereafter at the various district headquarters. He said that it was important that the cattle population which equalled the human population should be reduced and better strains developed. It was here that all animal lovers particularly those running cattle farms could play a vital role. He said the better strains of cattle would be healthier and thereby produce more milk which was needed by everyone. He said it was upto the people to start more co-operative milk societies in the various districts so that they could meet the needs of the people of those areas and if possible could also transport excess milk produced to Madras to help in meeting the milk shortage in the City.

Over 500 head of cattle, 100 sheep and 500 specimens of poultry were on exhibition

The Hindu: February 26, 1961.

Shipments of Hides and skins

Shipments of hides and skins for the first fortnight which totalled 1,454 bales were as follows: 581 bales tanned cow hides, 38 bales tanned cow calf skins, 26 bales tanned buffalo hides, 117 bales tanned buffalo calf skins, 58 bales tanned goat skins, 75 bales tanned sheep skins to the U.K., 5 bales tanned cow hides, 30 bales tanned cow calf skins, 48 bales tanned buffalo calf skins, 169 bales tanned goat skins, 102 bales tanned sheep skins to the Continent; 29 bales tanned buffalo hides, 15 bales tanned buffalo calf skins, 5 bales tanned goat skins, to the U.S.A., 2 bales tanned goat skins, 73 bales tanned sheep skins to Japan; 7 bales tanned goat skins, 53 bales tanned sheep skins to New Zealand; 9 bales tanned sheep skins to Australia; 12 bales tanned cow hides to Berbera.

The Mail: February 26, 1961.

Sheep farming

Valuable work in Nilgiris

The Government of Madras have been evincing great interest in the development of sheep farming and the woollen industry and as an initial step in this direction they started a Sheep Farm and a Wool Analysis Laboratory near Ootacamund ten years ago. The selection of Ootacamund was influenced by the fact that the renowned Wenlock Downs in the neighbourhood of the town afforded good grazing facilities for the sheep for a major portion of the year. Another reason for the location of the Sheep Farm near Ooty was that local sheep could be upgraded by the introduction of large quantities of British sheep blood in order to enable them to yield fine wool.

One of the difficulties that were experienced in the development of sheep farming here at the beginning of the scheme was that the average wool yield per animal per year was only about one pound, which was far below the minimum, although the sheep were found to be hardy and were able to withstand the rigours of the cold climate satisfactorily. By adopting selective breeding and improved sheep farming methods, the body weight and other qualities were improved, but the wool yield continued to be low. The Indian Council of Agricultural Research, who were approached for help in this matter, sanctioned a scheme of cross-breeding of the indigenous sheep with imported rams like Romney Marsh and Cheviot sheep. The Romney Marsh Rams were first imported from New Zealand in 1955 and since then both cross-breeding and selective breeding have been carried out in this Farm. Recently the Farm has also received some Russian rams which are similar to the Romney Marsh rams. At present, quite a large number of lambs, the progeny of these imported breeds of rams are available at the Farm.

The Farm staff have been paying a great deal of attention to the development of pasture right from the beginning and today one can see acres and acres of green pasture land surrounding the Farm. By hard and consistent research they have succeeded in evolving certain varieties of grass which can resist the biting and destructive frost during the winter.

With a view to enabling the villagers interested in sheep breeding to derive some benefits from the valuable work done in this Farm over 30 cross-bred rams are distributed to them annually

and this work is done in collaboration with the Block Development Officers in the Nilgiris District. They have also trained Flockmen to assist the villagers in the various sheep breeding operations like shearing, dosing and treatment of the animals free of cost. A Poultry Demonstration Centre is also functioning in this Farm in order to encourage poultry in the Nilgiris which is considered highly deficit in this respect.

The sheep breeding scheme has been sanctioned by the State Government only upto the end of 1962 and it is understood that the question of extending it further is under the active and serious consideration of the Government. This Farm, apart from playing a useful role in encouraging sheep breeding among the ryots and thereby helping them to supplement their income from agriculture, has proved a great tourist attraction since a large number of visitors to Ooty never fail to go there—it is about five miles from the town—and get themselves acquainted with its working.

The Hindu: February 28, 1961.

REVIEW

SCIENCE AND ART IN LEATHER MANUFACTURE. By A. G. Ward, pp. 20. (Leeds University Press, Great Britain, 1960). Price 2s. 6d.

The Leeds University Press has brought out an interesting booklet "Science and Art in Leather Manufacture" based on a lecture by Prof. A. G. Ward.

Prof. Ward has dealt with the extreme antiquity of tanning process, the unique character of leather, the development of the leather industry from prehistoric times through successive phases of manually making leather as a full time community occupation, improvement of quality through the Guild system, and the scientific approach and mechanisation which brought in their train increasing standardisation, newer materials and methods. Yet, even now the leather industry continues to be a craft industry, the skill derived from experience directing the processes and finding the products. The various efforts to unravel the complex nature of the skin and the unique character of leather through most modern techniques like X-rays and electronmicroscopy are only beginning to provide answers and the need for extending basic research to this craft industry is stressed.

Y. NAYUDAMMA

C.L.R.I. NEWS

Dr. Y. Nayudamma, Director, attended (1) the meeting of the Association of Principals of Technical Institutes at the P.S.G. College of Technology, Coimbatore, on February 9 and 10, 1961, (2) the meeting of the Quality Control and preshipment inspection of various goods exported from India held at Madras on February 2, 1961 and (3) the meeting of the Board of Directors of the Mysore Chrome Tanning Co., at Bangalore on February 22, 1961.

Dr. Y. Nayudamma, Director, visited Hyderabad on February 28 and March 1, 1961, and held discussion with Sri Konda Lakshman Bapuji, Minister for Small Scale Industries, and the Director-General, Scientific and Industrial Research, regarding setting up of an Extension Service Centre of the C.L.R.I. at Hyderabad.

Dr. Y. Nayudamma, Director, Dr. S. K. Barat, Assistant Director and Dr. S. N. Sen, Senior Scientific Officer, attended the meeting of the Southern Regional Committee of the Indian Council of Agricultural Research held at Madras from February 23-25, 1961.

Dr. S. K. Barat, Assistant Director, has been nominated as a member on the Sub-Committee constituted by the Committee of Administration of the Leather Export Promotion Council to consider the issue of Essentiality Certificates for importing tanning machinery, spare parts etc.

Mr. N. S. Mani, Senior Scientific Officer, attended the meetings of the Committee set up to consider the draft export plan for the Third Five Year, 1961-66.

Dr. D. Ramaswamy, Senior Scientific Officer, has been nominated as representative of the C.L.R.I. on the International Committee of Electro-chemical Thermodynamics and Kinetics.

PRESS & REGISTRATION OF BOOKS ACT

Registration of Newspapers (Central) Rules, 1956 FORM IV (See Rule 8)

Statement about ownership and other particulars about the Bulletin of the Central Leather Research Institute.

1. Place of Publication .. Adyar, Madras-20.
2. Periodicity of its Publication .. Monthly.
3. Printer's Name .. G. Srinivasachari.
Nationality .. Indian.
Address .. 21, Narasingapuram Street, Mount Road, Madras-2.
4. Publisher's Name .. N. Subramanian.
Nationality .. Indian.
Address .. Central Leather Research Institute, Madras-20.
5. Editor's Name .. Y. Nayudamma.
Nationality .. Indian.
Address .. Director, Central Leather Research Institute, Madras-20.
6. Name and addresses of individuals who own the newspaper and partners or shareholders holding more than one per cent of the total capital .. Central Leather Research Institute (C.S.I.R.).

I, N. Subramanian, hereby declare that the particulars given above are true to the best of my knowledge and belief.

Date: 1-3-1961.

(Sd.) N. SUBRAMANIAN

Signature of Publisher.

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

"Registered No. M. 7050."

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For further information please contact

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