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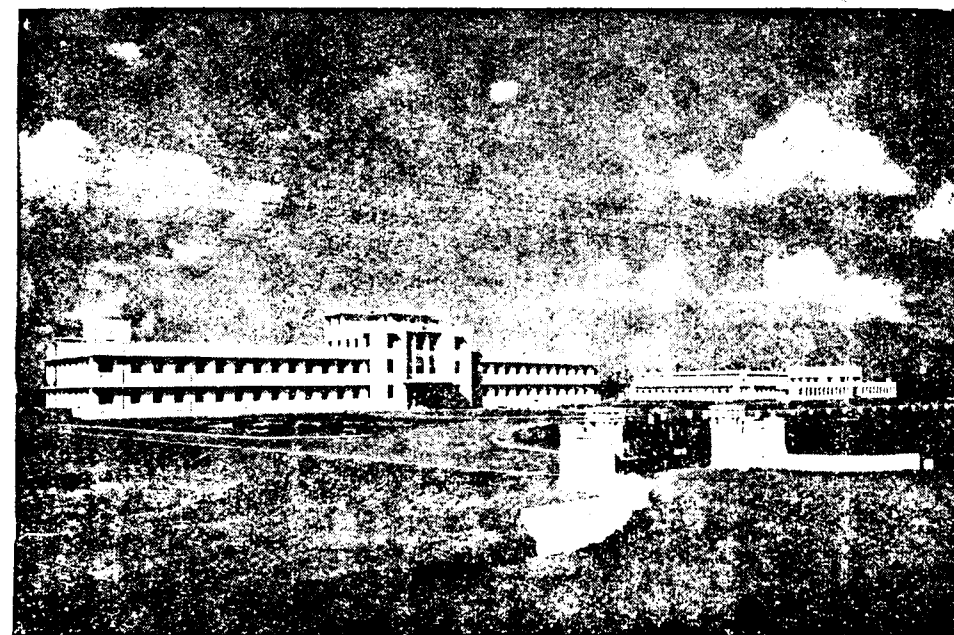
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PREPARATION AND TANNAGE WITH NONIONIC CHROME LIQUORS

BY

Y. NAYUDAMMA, S. P. SINGARAM & D. RAMASWAMY
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SUMMARY

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A method of preparation of 95-98% nonionic chrome liquor using calgon for masking is described the anionic chrome complex being removed by ion exchange resin. The stability of such a liquor over a range of pH from 2.0-7.0 was studied. Decomposition was noticed only beyond a pH of 5.5. Tanning experiments showed maximum fixation of 5.4% Cr_2O_3 per 100 g. of hide substance at a pH of 3.5; a shrinkage temperature of 68°C only was obtained using pelt as the substrate. Studies on the mechanism of nonionic tannage with different substrates like modified collagen showed that the sites for fixation of Cr were possibly the side chain nonionic groups of collagen.

Introduction

Earlier studies¹ on retannage of chrome leather with vegetable tans indicated that the type of initial tannage affected the properties of retanned leather to a large extent. Tannage with nonionic chrome liquors has by its very nature a special interest. The first difficulty in effecting a nonionic chrome pretannage was in preparing a hundred percent nonionic chrome liquor due to gel formation, precipitation and instability to ageing. Hence the conditions for preparation of stable nonionic liquors had to be standardised. The present paper deals with (i) the preparation of nonionic chrome liquor by calgon addition, (ii) the tanning studies with such liquors and (iii) the mechanism of nonionic chrome tannage.

Experimental

Preparation of nonionic chrome liquor:

When masking agents are added to 33⅓% basic chrome liquor, they penetrate into the coordination sphere and reduce the char-

ges of the chrome complex thereby decreasing the cationic chrome content. If selected masking agents like sulphite are used, the resulting liquor contains more of neutral complex carrying no charge. It was observed by Gustavson² and others³ that when sodium sulphite in the mole ratio of 2.5 of sulphite to one of Cr_2O_3 was added to neutral salt-free basic chrome liquor, it was possible to obtain a liquor containing as much as 86% chrome in the non-ionic form.⁴ Attempts were made to increase the nonionic Cr content by altering the mole ratio of sulphite to chrome and by use of ion exchange resins. However, stable liquors containing higher percentages of chrome in the nonionic form could not be obtained. Hence alternative masking agents were tried.

Masked nonionic chrome liquor with calgon (sodium hexametaphosphate $(\text{NaPO}_3)_6$):—Though it is known that calgon masking reduces the charge of the chrome complex, no detailed investigation seems to have been carried out. Preliminary experiments showed that calgon masking gave a high percentage of nonionic chrome complexes and hence a detailed study was undertaken with calgon masked chrome liquor. It was found that at a mole ratio of Cr_2O_3 : calgon = 1:0.8, a liquor containing 94% of the chrome complexes in nonionic form was obtained as analysed by paper electrophoresis⁵ as well as by standard ion exchange method. This liquor, however, was unstable yielding a gel when aged for a few days. If the mole ratio of calgon to chrome was increased to 1.2:1, the calgon masked chrome liquor was quite stable but had only 78% of the chrome content in nonionic form. Attempts were made to remove the anionic chrome complex; ion exchange resins were employed for this purpose. The calgon masked chrome liquor was shaken with the required quantity of anion exchange resin (Amberlite IRA—400), in the chloride form. The resultant liquor after filtration showed on analysis 95-98% chrome complexes in the nonionic form; also the liquor was stable over a long period and therefore could be employed for studies on tannage.

Stability of liquor containing nonionic chrome-calgon complex:

In order to ascertain whether the nonionic liquor owed its stability to the electrolytes present, the liquor was dialysed against distilled water using a collodion membrane. Rapid gel formation probably due to aggregation resulted showing that the liquor was stable only in presence of electrolytes. That electrolytes contribute to stabilising of basic liquors has been reported recently.⁶

Instead of the shaking method where only an equilibrium between the exchanger and the solution was obtained, the ion exchange resin was taken in a column so as to completely remove the anions; the chrome got precipitated in the column itself.

It has been pointed out by Gustavson⁴ that the stability of nonionic liquors under the conditions of tannage as assumed by Shuttleworth⁷ is open to question. In order to be reasonably definite about the stability of the liquor, the effect of pH was studied. The chrome-calgon liquor was adjusted to equilibrium pH values of 2.0, 4.0, 5.5 and 7.0 and analysed electrophoretically. It was experimentally found that the liquors showed almost the same nonionic content upto pH of 5.5. Hence the possibility of decomposition occurring under the conditions of tannage due to pH change is rather remote.

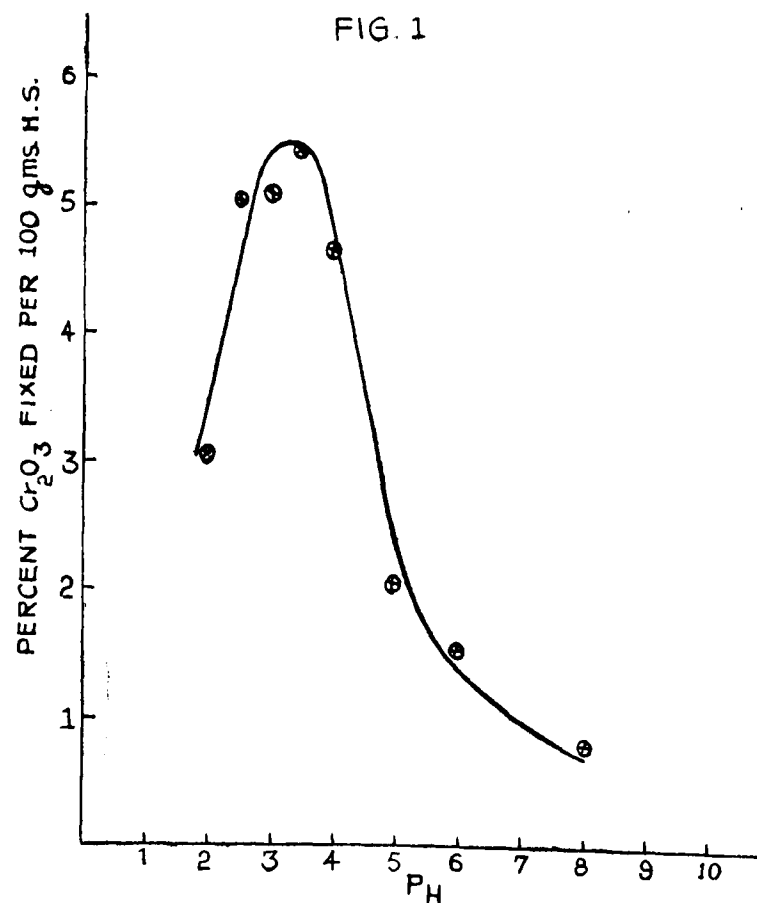
Tanning experiments with nonionic chrome liquor:

Effect of pH: Eight batches of hide powder each equivalent to 3 g. dry weight were soaked in 30 ml. of distilled water for 2 hours in the shaker; calgon masked nonionic chrome liquor prepared and aged for one week was then added equivalent to 6% Cr_2O_3 on dry hide powder basis. The pH was adjusted to 2.0, 2.5, 3.0, 3.5, 4.0, 5.0, 6.0 and 8.0 respectively by the addition of normal hydrochloric acid or normal sodium hydroxide solution. The pH values were adjusted until equilibrium was attained which was completed within 48 hours. Then the hide powder samples were suction filtered, washed thrice with distilled water, adjusted to different pH values, air dried and analysed for moisture, hide substance and fixed chrome.

Fig. 1 shows the plot of Cr_2O_3 fixed per 100 g. of hide substance against the different pH values. It is seen from the graph that the maximum fixation takes place around pH value of 3.5*. In order to ascertain further whether the nonionic liquor was stable throughout the experiment, exhaust chrome liquors of the experiments at different pH values were filtered and analysed

*The referee had suggested determination of phosphate in order to find out whether the reaction is a form of calgon tannage. On analysis of the leather sample at maximum Cr_2O_3 fixation (5.4%), P_2O_5 fixation worked out to be 14.7%. Since calgon fixation does not ordinarily exceed 5-6%, it has been concluded that the phosphate is associated with the chrome complex and the reaction is between chrome and reactive sites of collagen.

electrophoretically. It was found that no appreciable change in charge was observed at pH values 2 and 4. However, at higher pH values, significant change in the ionic character was observed. At the highest pH value 8.0, the decomposition was to the extent of 50% and was into both cationic and anionic forms.



Shrinkage temperature and nonionic tannage:

It is well known that a small increase in shrinkage temperature is obtained with nonionic liquors. Shrinkage temperature as low as 83°C was obtained with nonionic sulphite liquors. With nonionic chrome-calgon liquor, the shrinkage temperature found by experiment at pH 3.5 with 5.4% Cr_2O_3 fixed per 100 g. of hide substance was only 68°C, registering an increase of only 6°C over T_s of the pelt. The same increase was obtained with hide powder, a value of 58°C being obtained with the microshrinkage

apparatus. The comparatively insignificant increase in shrinkage temperature points to the very weak binding of the nonionic chrome complex at the reactive sites of collagen.

Mechanism of tannage with nonionic chrome liquors:

It is evident from T_s measurements that the tanning is attributable to only the residual valency forces as suggested by Gustavson^{8,9} since with any other type of linkage, higher shrinkage temperatures ought to be obtained especially with mineral tanning agents like chrome. It has been recognised that part of the chromium fixed in normal chrome tannage is in the form of adsorption compounds held by secondary valence forces.^{10,11} The reactive sites responsible for the binding of nonionic chrome should essentially be nonionic as already suggested by Gustavson.⁴ However, it has been found that hydrated polyamide does not fix any nonionic chrome-calgon complex. This may indicate that the peptide groups may not be necessarily involved in the fixation of nonionic chrome. The other nonionic sites in the collagen are hydroxyl groups in the side chain of the amino acid residues. Green¹² suggested that the hydroxyl groups also participated in the chrome tannage. The participation of hydroxyl groups in nonionic sulphito-chromium sulphate tannage has originally been suggested by Gustavson^{13,14} from evidence obtained from heat-denatured and urea-pretreated collagens and polyamide with nonionic sulphito-chrome liquor.* To determine the further role of hydroxyl groups, the fixation of nonionic Cr on acetylated collagen and elastin was studied.

Acetylation of collagen was carried out by treatment with acetic anhydride in acetic acid in presence of formic acid for 7 days.¹⁵ The resulting acetylated hide powder after dehydration, grinding and air drying showed 1.45 meq. of acetyl content by standard method.¹⁶ The modified hide powder was tanned with nonionic chrome calgon liquor exactly as normal hide powder and analysed for fixed chrome, hide substance and shrinkage temperature. The results are given in table I.

It is seen from the data that acetylation reduces the fixation by 45-50% without conferring any increased thermal stability as

*The need for differentiation between cationic, nonionic and anionic Cr tannages has been questioned by the referee. However in view of Gustavson's work on nonionic Cr tannage and on the basis of the present work, such differentiation appears to be necessary. Further work may clarify this aspect.

compared to normal hide powder. The procedure adopted for acetylation brings about both N- and O- acetylations; however, since the amino groups are unlikely to take part in nonionic tannage it is probable that the reduction in fixation is due to nonavailability of the sites provided by hydroxyl groups. However, it is assumed that the lowering of fixation brought about by the decrease in swelling of acetylated collagen is not so great as to explain the effect observed.

TABLE I

Substrate	pH	Fixed Cr_2O_3 /100 g. of H.S.	T.
Normal hide powder	2.5	5.0	55-8°C
-do-	3.5	5.4	56-8°C
Acetylated hide powder	2.5	2.49	44-6°C
-do-	3.5	2.95	46-8°C
Normal hide powder	—	—	50-°C
Acetylated hide powder	—	—	40-4°C

Further confirmation on the role of hydroxyl groups as sites for fixation of nonionic chrome was sought by taking as substrate elastin fibre which resembles collagen in most respects except for the presence of hydroxyproline. Tanning experiments showed that elastin fixed as low as 0.64% Cr_2O_3 /100 g. of hide substance as against 3.4% Cr_2O_3 /100 g. of hide substance by collagen under identical conditions suggesting the participation of side chain hydroxyl groups as sites. The lower content of ionic groups like aspartic, glutamic, lysine, arginine, etc., in elastin cannot possibly account for the lowering of fixation on nonionic chrome due to their ionic nature.

Hide powder, when treated with lyotropic salts, is known to fix more nonionic Cr^{17} ; however, this was not observed with non-ionic Cr calgon liquor. The fixation of chrome was 3.26 g. Cr_2O_3 /100 g. hide substance with lyotropic salt treated hide powder as against 3.47 g. with normal hide powder under the same conditions. The reason for the discrepancy between chrome sulphite liquor and chrome calgon nonionic liquor is not quite clear. Though the former liquor was not completely nonionic, the disparity in

fixation is probably due to the nature of the ligand. Further, the nonionic Cr tanned collagen was stable to treatment with 8M urea. Prolonged treatment for 48 hours stripped only about 5% of the fixed chrome showing thereby that the nonionic chrome is not probably fixed to those keto-imide sites which are liable to compete for hydrogen bond formation. However, it was found by experiment that esterified collagen fixed 22% more of chrome under the same conditions. This is in conformity with the findings reported in literature.⁴ It is evident that additional nonionic sites formed during esterification in the side chain are responsible for the increased binding of nonionic chrome. The shrinkage temperatures obtained with both lyotropic salt treated hide powder and esterified hide powder on nonionic tannage was 56-8°C compared to 44-6°C before tannage.

Hence it is concluded that the binding of nonionic chrome-calgon complex probably takes place at the nonionic centres in the side chains of polypeptide unit. Whether this initial binding by secondary forces leads to precipitation or gel formation within the fibre could not be established by the present studies, though the possibility exists as evident from dialysis studies of nonionic chrome-calgon liquors mentioned earlier. Further studies on other types of masking agents as well as mineral tanning agents are necessary before any generalization can be made on the mechanism of nonionic tannage as a whole.

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ESTIMATION OF THE DIFFERENTLY HELD ACID GROUPS IN CHROME TANNED LEATHER

(A Review)

BY

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Introduction

During chrome tanning, basic chrome complexes are considered to get bound to collagen. The basic chrome complexes present in the chrome liquor are generally represented as $[\text{Cr}_2(\text{OH})_2\text{SO}_4]^{++}\text{SO}_4^{--}$. It has been recognised¹ that on completion of chrome tannage, there are three possible types of acidity in chrome tanned leather, viz. (1) acid combined with basic groups of protein, i.e. 'protein bound acid', (2) acid complexly bound to the fixed chrome and (3) acid ionically bound to the fixed chrome. In the course of washing the chrome leather after completion of tannage, all these forms of acid groups are partly hydrolysed and partly removed along with the uncombined chrome. Further on subsequent neutralisation with mild alkali, of the undesired acids and soluble salts that are invariably present after chrome tanning, the different forms of fixed acid are likely to be partially neutralised. The extent to which these various changes occur in the fixed chrome complex have far reaching effects on the characteristics of the final leather. Hence an accurate knowledge of the distribution of these differently held acid groups is of utmost importance; it not only helps the proper understanding of the mechanism of neutralisation, but also leads ultimately to understanding the type of chrome complexes fixed and the mode of their fixation on collagen.

In 1920, Thomas² proposed a method for the estimation of acidity of chrome leather; this has been adopted as an optional method by the American Leather Chemists' Association. This method employs sodium dihydrogen phosphate to extract all the sulphate groups present in the leather. Distilled water extracts only the

neutral sulphate together with a small amount of free acid arising from hydrolysis which is corrected for by a separate blank titration. Though the method works out fairly well, it fails to give any information about the manner of distribution of acid sulphate in chrome leather. A method for estimating the total acid sulphate groups in leather by extracting with ammonia instead of sodium dihydrogen phosphate has also been suggested.³ This method has been adopted as the preferred method of the American Leather Chemists' Association. But this method too does not give a true picture of differently held acid groups. Furthermore, the results obtained by the phosphate method are of the same order as those obtained through ammonia extraction. Meunier *et al.*⁴ have suggested a method in which chrome leather is extracted with a known excess of sodium bicarbonate solution and the excess of bicarbonate is titrated. This method yields somewhat low results; further the method holds good for the freshly tanned chrome leather only. Atkin⁵ used a modification of the Procter-Searle method; this too does not give encouraging results. Riess *et al.*⁶ estimated the total acid present in Cr leather by ammonia-formaldehyde method. This method measures not only the sulphate groups, but also other acid groups such as formate; only the ammonium salts present in the leather also will be accounted as acid. Further, this method and the method put forth by Thomas (*loc. cit.*) lead to results of the same order of magnitude.

In 1926, Orthmann⁷ made the claim "that the chrome-acid collagen complex having a basicity of 66% will not submit to a further hydrolysis by action of water". Wilson *et al.*⁸ showed clearly that all the combined acid sulphate of chrome leather could be hydrolysed as free sulphuric acid on washing the leather with distilled or tap water for a period of 64 days, the basicity of the complex rising to 100%. Gustavson⁹ first attempted to distinguish between the sulphate groups attached to the protein and those combined with chromium. He clearly showed the difference in the rates of hydrolysis of the two forms of sulphate—sulphate bound with protein and that bound with fixed chrome complex and indicated that all protein bound acid was neutralised by suspending the leather in water and adding alkali in small increments, to keep the liquor just acid to an indicator. This diffusion neutralisation method though much favoured, has its limitations; it is time consuming and unless the diffused acid is removed immediately, disturbance of the equilibrium is likely to result, since the reaction is reversible. Hence Gustavson¹⁰ proposed to use pyridine to neu-

tralise the protein bound acid, thus accomplishing the determination more rapidly and easily. He assumed that the undisplaced acid was entirely in the form of chrome bound acid. Merrill *et al.*¹¹ showed that the pyridine method gave much higher values for protein bound acid than the "diffusion neutralisation method" and indicated that the amount of sulphate left after pyridine agitation would be determined by such arbitrary factors as the volume of solution employed, the concentration of sulphate in the solution and total percentage of the acid sulphate in the leather. They concluded that pyridine displaced a part of the chrome bound sulphate and also presented evidence in support of the view that the diffusion neutralisation method gave more nearly correct results. A few minor changes in Gustavson's original "diffusion neutralisation" procedure were carried out, but these were relatively unimportant. Later Merrill *et al.*¹² showed that there was very little difference in the degrees of hydrolyzability of protein bound acid and part of the chrome bound acid and that an equilibrium apparently existed between the two forms of acid. They concluded that protein bound and chrome bound acids were in labile equilibrium, and that precise differentiation between the two forms of acid sulphate was not possible. In the chrome bound acid, at least two different modes of attachment have to be considered; (i) acid sulphate held directly by the central atom constituting the internal sphere and (ii) acid sulphate group held outside by electrostatic forces as "ionogens or gegenions."¹³ Gustavson¹⁴ explained the higher values of protein bound acid obtained by Merrill *et al.*, as due to the removal of externally held acid groups in the pyridine treatment. According to him, the ionically held sulphate groups attached to chromium should offer less resistance to neutralising agents like pyridine than the acid groups in direct combination with chromium. But Stiasny *et al.*¹³ were rather inclined to believe that the pyridine method tended to give too high values for sulphate groups, as the sulphate groups held as ionogens outside the complex might not be removed by the pyridine. In order to make the pyridine method of greater application in control work, they modified the procedure somewhat, adopting a titrimetric procedure for the estimation of protein bound acid. The complexly held acid groups were obtained by subtracting the amount of sulphate titrimetrically obtained from the amount of combined sulphate present in the original leather before pyridine treatment.

Küntzel *et al.*¹⁵ too suggested a method for differentiating the various acid radicals; total acid (A) was determined by ammo-

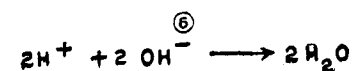
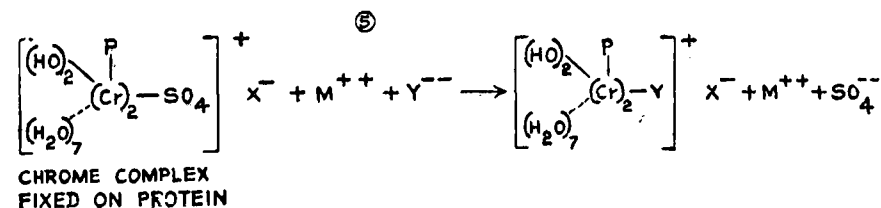
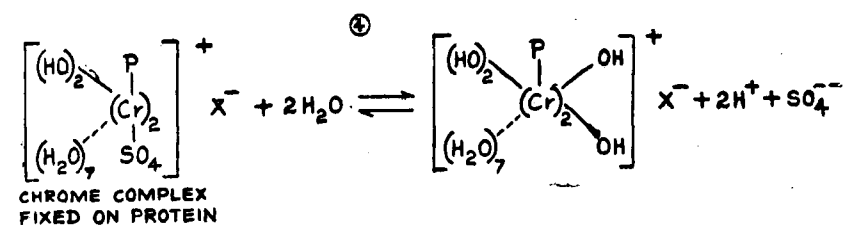
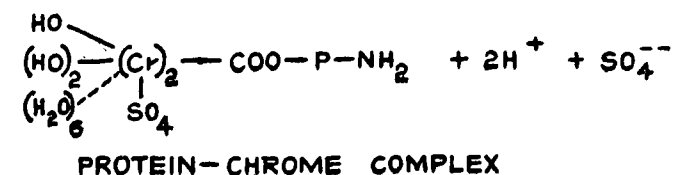
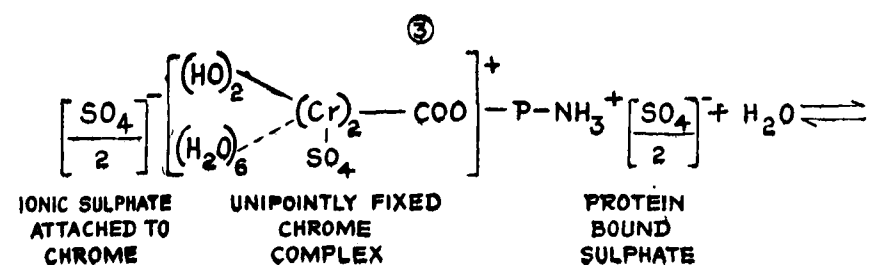
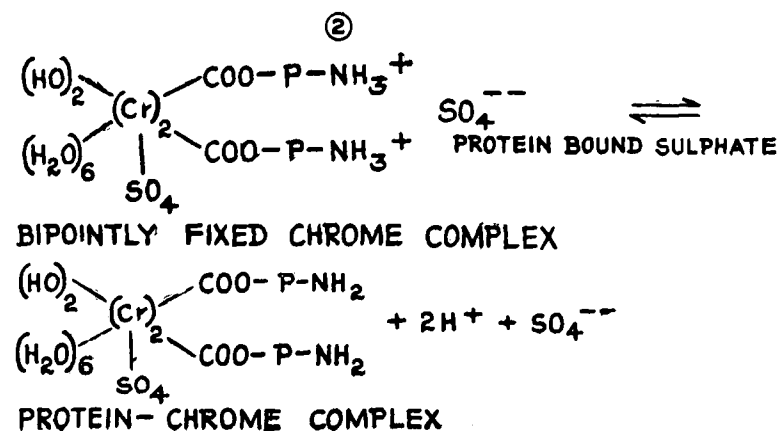
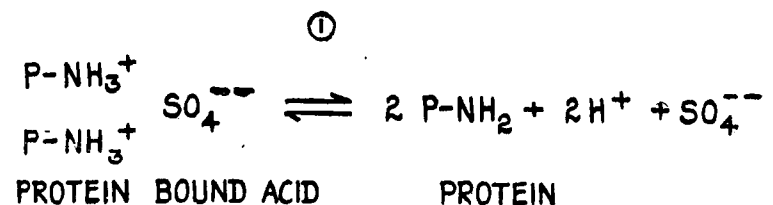
nia-formaldehyde method, protein bound acid, (B), as the difference in absorption of acid between untanned hide powder and chrome tanned leather, acid ionically bound to chrome (C), by means of a modified pyridine extraction method, deducting the value from the protein bound acid, and the acid complexly bound to chromium (D), as the difference between (A) and the sum of (B) and (C). This method, however, has not proved to be quantitative as the assumed maximum acid binding capacity of the hide powder is much too low. Combined acid was obtained as the difference between two approximate values not giving the true value for the chemically fixed acid as distinct from that for physically adsorbed acid. Further, no insight is obtained into the distribution of acid groups in the original unaged leather. Theis¹⁶ estimated the different acid groups by the iodine-iodate-thiosulphate method. As the result of a comparative study of the different methods in use for estimation of acid content in leather, Küntzel *et al.*¹⁷ concluded that (i) the Theis method¹⁶ gave incorrect results and (ii) the errors involved in the methods of Riess and Papayannis⁶ and Thomas² were of the same order of magnitude.

The diffusion neutralisation method though much favoured, has its limitations; it is time consuming and unless the diffused acid is removed immediately, disturbance of the equilibrium is likely to result since the reaction is reversible. McLaughlin *et al.*¹⁸ in their survey, concluded that the diffusion neutralisation method as modified by Merrill and coworkers was the soundest, despite its limitations, for differentiating protein and chrome bound acids. Later, it has been reported¹⁹ that the complexly held sulphate groups in ordinary chrome leather are not removed by pyridine as a rule, if this is applied as a 4% solution for 1-4 hours. Spectrophotometric and dye fixation studies²⁰ on the effect of adding pyridine to chrome complexes indicated changes in the chrome complex on treatment with pyridine at pH values from 3 to 5. This lends support to the earlier findings of Merrill *et al.* Hence, in both these methods, viz. diffusion neutralisation method and pyridine method, quantitative distinction between chrome bound and protein bound acids is not possible. Further the hydrolysis may not be complete when fixed chrome is present in large quantities.

Recently, Nayudamma and Theis²¹ have proposed a method for the estimation of protein bound acid, which is a further modification of diffusion neutralisation method originally proposed by Gustavson. This method employs 0.1N potassium chloride solution; the

diffused acid coming out from the leather is titrated against dilute sodium hydroxide to an end point at a pH 4.0-4.3. It has been clearly indicated that the chrome complex is stable at pH 4.0-4.3. Some of the experiments²⁰ carried out in this Institute have indicated that though the method is quite accurate in finding the protein bound acid, it fails, to give the value for the truly complexly held sulphate groups of chrome after neutralisation of protein bound acid to pH 4.3. It has also been found that the value of protein bound sulphate is more than what could be accounted for as the protein bound acid; this has been attributed to the entry of chloride groups replacing the sulphate present in the complex due to mass action effect. An improvement in the pyridine method for the differential estimation of ionic sulphate and complexly held sulphate groups using hexamethylene tetramine (urotropine) instead of pyridine was attempted. The results obtained by employing hexamethylene tetramine solution of concentration 4% have been found to be of the same order as those obtained by pyridine method. Yet another approach to the problem has also been made recently with the help of statistical method to get an equation for getting protein bound and chrome bound acids.²²

Thus all these methods so far adopted have failed to give true picture of the differently held acid groups. The following reactions need to be taken into account during estimation.



In the above equations, X is the aquomolecule or basic OH group and MY is the neutralising agent, M being the metallic part and Y being the anion which may be either monovalent or bivalent. If the anion of the neutralising agent is bivalent, one molecule of the neutralising agent will be sufficient for replacing all the complexly held sulphate groups, provided the anion has penetrating tendency based either on strong coordinating ability towards chrome complex or on mass action effect.

From the reaction mechanisms formulated above as taking place during estimation or neutralisation of the acidity of the chrome leather, two points will be quite clear.

(i) Simultaneous hydrolysis of chrome bound sulphate (ionically held and complexly held) with the hydrolysis of protein bound acid, thus giving to rise high value of protein bound acid.

(ii) Replacement of the chrome bound sulphate groups by the anion of the neutralising or protein bound acid estimating agent.

In developing such a method for the separation of protein bound and chrome bound acids, the elimination of undesirable effects as stated above should be borne in mind for accurate quantitative determination. Recently, a nonaqueous titration technique has been put forth for titrating any acid or alkali which presents difficulties in aqueous media.^{23, 24}

In 1946, Palit²⁵ showed that salts of weak acids can be titrated very accurately in ethylene-glycol and isopropanol medium. The salts of any weak acid acquire high basic strength, when dissolved in glycol and isopropanol medium and can be titrated against hydrochloric acid or perchloric acid in the same solvent mixture. Burton *et al.*²⁶ applied this technique for estimating the acidity of vegetable tanned leather. The method employs a known excess of sodium acetate in glycol and isopropanol medium (1:1) in which the vacuum dried leather sample is agitated for 48 hours and the excess acetate remaining behind is titrated against standard hydrochloric or perchloric acid in the same solvent mixture potentiometrically using glass and calomel electrodes. Selection of a suitable salt of a weak acid in the glycol-isopropanol medium which should neutralise only the protein bound acid present in the system without causing any detrimental effect to the existing chrome complex may be satisfactory for the differential estimation. Palit²⁵ showed that even the salts of inorganic acids of the type -XOO, where X stands for any electro-negative element, can be titrated using glycol-isopropanol medium. Since acetate is capable of penetrating into the chrome complex present in the leather, Burton's method²¹ cannot be applied for the differential estimation of protein bound acid and chrome bound acid.

It has been shown that boric acid and borate have no influence on the basic chrome complexes present in the liquor²⁷ as well

as in the leather.²⁸ Borate buffers have also been used for studying the isoelectric point of chrome tanned leather, because they have no complexing ability. The experiments²⁰ using sodium borate in ethylene glycol and isopropanol medium carried out in this Institute have shown that borate gives a sharp and accurate end point on titrating against standard hydrochloric acid in the same solvent mixture. It has also been found that the non-aqueous titration technique using sodium borate in glycol and isopropanol medium holds good in estimating protein bound acid present in untanned collagen subjected to treatment with varying amounts of acid and neutral salt to prevent swelling.²⁹ As the borate present in the solvent mixture directly neutralises the protein bound acid, the hydrolysis of chrome bound sulphate groups that occurs in aqueous medium is suppressed. This is also quite evident from getting the same end point for 33% basic chrome sulphate extract (B and C) as compared to the blank under identical conditions. The extension of this study to estimation of protein bound acid and chrome bound acid differentially in the case of chrome leather has also been successfully accomplished in this Institute. The results so obtained will be published later. But the problem of differentiation of ionic sulphate attached to the chrome complex and complexly held sulphate groups still remains unsolved; however, attempts have been made to distinguish in a qualitative manner.

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RESEARCH BEARS FRUIT

Process for the Manufacture of Hockey Ball Leather* (Zirconium tannage)

BY

T. S. K. MAHADEVAN AND P. S. VENKATACHALAM

Introduction

Leather intended for manufacture of hockey balls should have good surface whiteness with a white cut, the surface having great impact and scuff resistances and a reasonable degree of resistance to wetting; other properties desired are good tensile strength, stitch tear resistance, resistance to spueing in wet weather and fastness to light.

The traditional tannage for hockey ball leather is with alum and salt; these leathers have obvious limitations taking in view the above requirements. As a result of intensive study, an improved process has been now developed by the Institute for the production of white leathers by zirconium tannage; the leather so obtained has proved satisfactory in respect of all the above characteristics.

Raw material:

Wet salted cow hides of the weight range of 14-18 kg. (30-40 lb. approximately) without grain defects and deep flay-cuts are employed. The raw material chosen should be capable of giving leathers with a final thickness of more than 2.5 mm, with a defect free grain.

Soaking:

The hides are washed in two changes of water (400% float) for 10 minutes duration and then soaked in a slightly acidic bath of the following composition:

Water	.. 400%	} On the wet salted weight of hides.
Sulphuric acid (commercial)	.. 0.5%	
Salt	.. 3.0%	

After 4 hours' soaking, the hides are taken out, piled to

*Process demonstrated at C.L.R.I. in April/May 1962.

drain and the soaked weight noted. Then they are given a wash before being sent to the lime yard.

Note : The object of giving the acidic bath is to remove the salt stains, if any. Care should be taken to see that the pH of the soak does not go below 4.00. If the hides are too dry, an overnight soaking in the above bath may be given. If the stock contains too much flesh, it is better to give a green fleshing before taking it to the unhairing bath.

Liming:

The soaked hides are cut into sides and taken to liming bath prepared as follows:

Sodium sulphide (50% purity) ..	1%	} on soaked weight.
Slaked lime paste ..	5%	
Twice used straight lime liquor (old) ..	200%	
Fresh water ..	200%	

The sides are handled and left in the liquor for 3 days. Handling is done twice daily. On the 3rd day, they are unhaird, washed, scudded and taken for reliming.

Reliming:

Reliming is done using the following:

Slaked lime paste ..	3%	} on soaked weight.
Water ..	400%	

The sides are handled in this for 2 days. After 2 days' reliming, the sides are taken out, fleshed and washed well.

Note : It is preferable to give a lime splitting to a thickness of 3.5 mm. thickness at this stage, if a splitting machine is available. Alternatively, hand fleshing to a uniform substance has to be ensured.

After this the pelt weight is noted and the limed pelts are taken to deliming after scudding.

Deliming:

Deliming is done in a tub using the following:

$\frac{3}{4}$ % boric acid	} on pelt weight.
200% water	

The stock is trampled for 2 hours and left overnight in the bath. Next day, it is taken out, scudded well, tested for completion of deliming with phenolphthalein indicator.

Note : The above liming and deliming has been so adjusted as to obtain a clean white pelt with a moderate opening up of the structure.

After deliming and washing, the sides are taken for bleaching.

Bleaching:

Bleaching is carried out in a tub with:

Hydrogen peroxide (100 vols.) ..	1%	} on pelt weight.
Liquor ammonia ..	$\frac{1}{4}$ %	
Water ..	200%	

The sides are handled in this tub for $\frac{1}{2}$ hour and then left in the bath for 3-4 hours and covered with a clean gunny bag. They are taken out of the bleaching bath when the bath becomes pale yellow in colour, washed well and taken to pickling.

Pickling:

The pickle bath is made up in a tub with:

Sulphuric acid (commercial) ..	1.5%	} on pelt weight.
Common salt ..	10%	
Water ..	100%	

The sides are handled in this pickle bath and left in it overnight. Care is taken to see that the pH of the bath is kept below 2.5.

Note : It is preferable to use 1% sodium citrate and 9% common salt and sulphuric acid 1% and formic acid 0.5% instead of the recipe given above, subject to the availability of the same.

Next day, the sides are tested for completion of pickling using bromophenol blue indicator and taken to tanning.

Tanning:

The tanning material used is commercial "Zircotan N" (Rohm & Haas). The quantity of Zircotan used is 15% on the pelt weight of the stock. The same is added in 3 equal instalments, adding one instalment each day. First 5% of the Zircotan N is dissolved in a small quantity of the pickle liquor itself and added to the pickle bath in the tub. The sides are handled well and left overnight. Next day, the sides are handled in the

same bath. On the third day, the second instalment of 5% of Zircotan is dissolved in a small quantity of the pickle bath, added to the same slowly and handled well. On the fourth day, the final instalment of 5% Zircotan is added in the same way. The sides are taken out, worked on a clean beam and returned to the bath. The sides are handled in this bath daily for a period of 7 days and tested for completion of penetration of the tanning salt. For this a small cut piece is taken from the tight portion of the side, dried in the shade and examined for untanned streak, if any. The cut section should not show any glossy layer in the middle. The shrinkage temperature of the pelt should be about 70°-72°C. After complete penetration, the bath is basified using the following mixture:

Sodium acetate (commercial)	.. 2 Parts	} quantity 3-4% on pelt weight.
Sodium bicarbonate (commercial)	.. 1 Part	

The above mixture is dissolved in the minimum quantity of water and added in instalments to the tanning bath. The basification is done gradually over a period of 2-3 days and finally the pH of the bath is adjusted to about 4.0. After basification, the sides are allowed to remain in the same bath for a couple of days more. The shrinkage temperature is about 98°C. Then the sides are taken out, washed well and piled overnight over a horse.

Note : The basification should be done as gradually as possible, as otherwise the zirconium salt which is very sensitive to drastic changes in pH will precipitate out. The basification mixture should be used in the given ratio, so that there will always be an excess amount of buffer salt present in the bath.

Next day, the sides are sammed to about 50% moisture content, the sammed weight is noted and the sides are taken for fatliquoring.

Fatliquoring is done in a tub using the following:

*Sarboline SS	.. 2%	} on sammed weight.
Coconut oil	.. 1%	
China clay (Kaolin)	.. 2%	
Titanium oxide	.. 1%	
Hot water (50°C)	.. 200%	

*Product of Fletcher Miller & Co.

The fatliquor is well emulsified in this bath along with the pigments and then the sides are handled in the same for 40 minutes by which time the fatliquor is absorbed by the stock. After fatliquoring, the sides are taken out and piled.

Next day, they are sammed, set well with a clean glass slicker and nailed on boards for drying.

When the sides are dry, they are removed from the boards, trimmed and buffed with 240 grit Aloxite paper. Final weight is noted after buffing.

The average yield is 40% approximately.

Note : (i) In the process given above, all the operations mentioned have been carried out in vats only in order to obtain a better grain pattern. This incidentally enables the small scale tanner also to adopt the same process, after making necessary adjustments. (ii) Though "Zircotan N" is at present an imported product, there is a good scope for developing zirconium tanning salts in India also as there are abundant supplies of raw material available.

Acknowledgement

The authors' thanks are due to Dr. T. S. Ranganathan, Senior Scientific Officer, Central Leather Research Institute, for the suggestions given by him in developing the process.

LETTER TO THE EDITOR

An electrical microbalance for fibres

Microbalances suitable for weighing single fibre have been developed to some extent in the past. Most of these use quartz spiral or torsional devices; some others employ the principle that the current to be passed through an electrical measuring instrument to bring the pointer back to its original position is proportional to the weight added to the pointer.^{1,2} Electrical microbalances are less time consuming than their mechanical counterparts. The present paper describes an electrical microbalance using the same principle as stated above but utilising an electrical circuit different from those of previous workers.

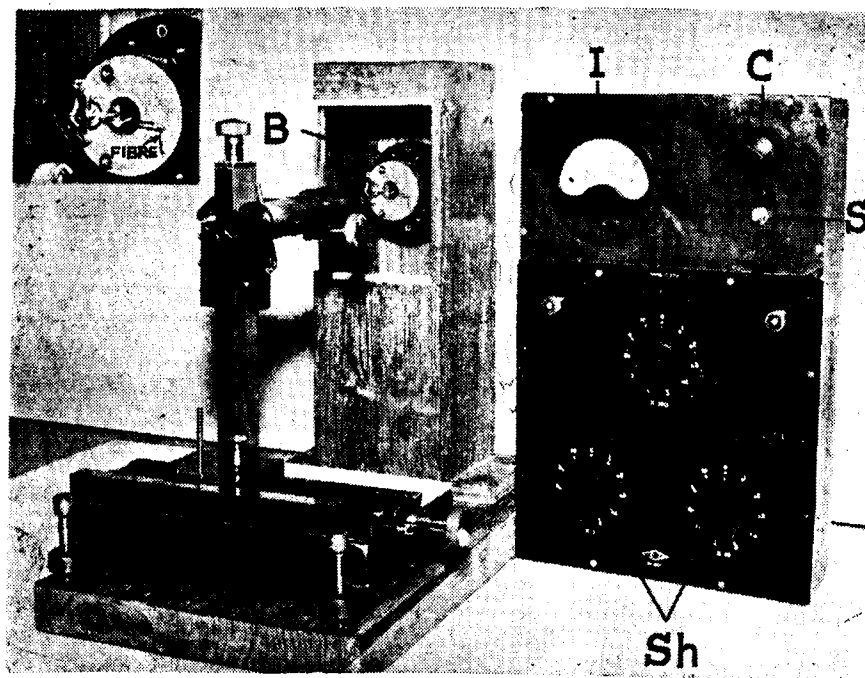


FIG. 1. The Microbalance

The microbalance is shown in fig. 1 and the circuit diagram is given in fig. 2. 'I' is a milliammeter in the range 0-1 μ A, 'B'

is a microammeter in the range 0-500 μ A, 'S' is a variable resistance in the range 0-680 ohms, 'C' is a variable resistance in the range 0-50,000 ohms and 'Sh' are shunts for the microammeter.

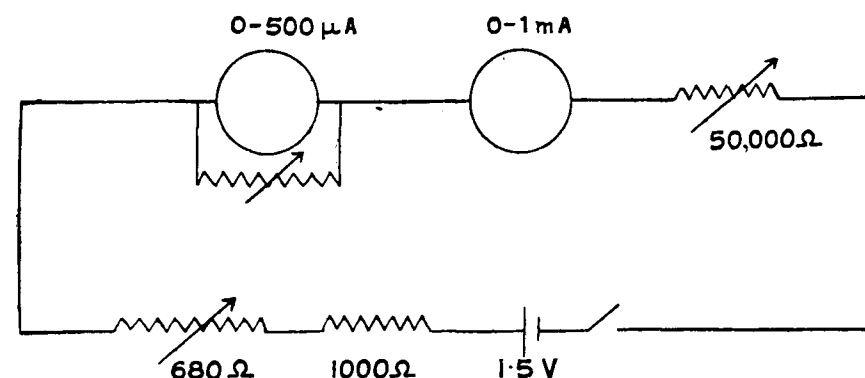


FIG. 2

The pointer of the microammeter 'B' is brought to the centre by counterpoising a small piece of thin metal foil. The meter is mounted in a wooden box lined with perspex on the inside in such a position that the pointer is horizontal. A travelling microscope is placed on a heavy base to which the meter mounting box is rigidly fixed.

In operation, the travelling microscope is focussed on the tip of the pointer of meter 'B' so that it coincides with the horizontal cross-wire. Keeping the resistance 'C' at its lowest value, viz., zero, the resistance 'S' is adjusted to give 1 μ A deflection. This standardises the total controlling current. Then the resistance 'C' is adjusted so that the meter 'I' indicates zero.

The fibre is suspended from the tip of the pointer as shown in the inset of fig. 1. A deflection depending on the weight of the fibre is observed. The control 'C' is now adjusted till the pointer in the meter 'B' returns to its initial position as seen through the travelling microscope. The current indicated in the meter 'I' is noted. The weight of the fibre is read from a calibration curve drawn with known weights and corresponding currents. The shunt value is chosen to suit the weight range.

The relationship between current and weight is linear and the sensitivity of the microbalance is of the order of a few micrograms.

C.L.R.I., Madras }
April 11, 1962. }

S. ANANTHANARAYANAN, (JR.)
N. RAMANATHAN.

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TECHNICAL SEMINARS

Growth effect of *Aspergilli* on tans and nontans of vegetable tan liquors*

BY

V. S. KRISHNAMURTHY

Little information is available about the preferential utilisation of tans or nontans of vegetable tan liquors by fungi. As a step in this direction, the effect of growth of eight species of *Aspergilli*, viz., *A. fumigatus*, *A. unguis*, *A. sydowi*, *A. terreus*, *A. candidus*, *A. niger*, *A. flavus* and *A. ochraceous*, on tans and nontans of wattle and myrob tan liquors representing the catechol and pyrogallol types respectively was studied. The cultures were harvested at various age levels—15, 30 and 50 days after inoculation in the case of wattle and 7, 15 and 30 days in the case of myrob; analyses of both inoculated and control liquors were carried out. For elucidating certain changes in the phenolic constituents brought about by mould growth, the appropriate myrobalan liquors were analysed by circular chromatography. This could not be carried out with wattle liquor as there was no good separation of the various components.

Species of *Aspergilli* grown on wattle liquor revealed certain characteristics by which they could be grouped under the following categories: (1) species preferentially attacking tans—*A. unguis*, (2) species preferentially attacking nontans—*A. fumigatus*, *A. sydowi* and *A. terreus*, (3) species attacking both tans and nontans—*A. candidus*, *A. niger*, *A. flavus* and *A. ochraceous*.

Parallel studies were carried out with myrob liquor. On the basis of the data obtained, *A. fumigatus*, *A. terreus*, *A. candidus*, *A. niger*, *A. unguis* and *A. flavus* appeared to affect the tan liquors in a more or less similar manner, preferentially splitting the tan molecules. *A. sydowi* and *A. ochraceous* were found not to have

*Summary of the talk given on March 6, 1962.

any pronounced effect on tans, the nontans getting destroyed gradually in time. The initial increase in nontan content in the case of *A. fumigatus*, *A. unguis*, *A. sydowi*, *A. terreus*, *A. niger* and *A. flavus* might be due to the conversion of tans into nontans. With the ageing of culture, the nontan content went down. This could be attributed to the utilisation of the latter also by these species. The chromatographic data showed that the component with R_f value 0.26 was destroyed completely in all the cases a fact which shows that this genus is specific for this particular constituent.

Further work on the identification and qualitative utilisation of various components of vegetable tan liquors by species of *Aspergilli* is being carried out.

Studies on arecanut tannins*

BY

S. BANERJEE

The distribution of tannins in various parts of areca palm has been studied; the maximum amount of tannins was found in the nuts. Arecanut tannins have been found to be purely of the condensed type. As regards the variation of tan content with the age of the nuts, it was observed that the total tannins gradually decreased after the nuts became tender.

The polyphenolic constituents of the acetone and alcohol extracts of arecanuts were examined chromatographically. The chromatograms revealed five spots, among which one was identical with D-catechin and the other with (+)leucocyanidin. The acetone of ethanol extract of arecanuts on repeated extraction with ether gave the fraction containing catechin which was then converted into acetyl derivative employing pyridine and acetyl chloride; finally, the product was crystallised from ethanol. The acetyl derivative thus obtained was identical in all respects with D-catechin acetate (m.p. 128-129°C).

* Summary of the talk given on March 16, 1962.

After the removal of ether solubles from the extract, the residue was taken up in ethyl acetate; from the ethyl acetate solution, leucocyanidin was obtained as white powder by fractional precipitation with petroleum ether. With diazomethane, it gave a tetramethyl ether (m.p. 147-148°C) which yielded a diacetate (m.p. 160°C). Oxidation of the tetramethyl ether with KMnO_4 yielded veratric acid. This study showed the presence in arecanuts of a new dextrorotatory isomer of leucocyanidin.

Arecanut tannins were found to be highly buffered with appreciable amount of salts of weak acids. Further they were found to exist in aggregated form as was evident from their rather high gelatin number. The high gelatin number of arecanut tannins might be responsible for their slow penetration through gelatin gel as well as into hides and skins. The hydrothermal stability of leathers tanned with arecanut tannins was found to be quite high.

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TANNERS' CORNER

The Central Leather Research Institute has been since its inception rendering technical aid to the leather industry through answering technical enquiries on specific problems. The number of such enquiries has been increasing year by year. In order that the information contained in the replies to the technical enquiries may be available to all those who have similar problems, this new feature "Tanners' Corner" has been inaugurated. Typical questions will be reproduced herein with the relevant answers. It is hoped that the industry will fully utilise this new feature and bring more and more of its problems for solution by this Institute.

Q. XV. A shipment of prime sheep skins (with London as destination) was found on arrival to be damaged by weevil *Dermestes vulpinus*.

(i) Are the skins likely to have been infected with this weevil before the bales left the godown or to have been attacked on board the steamer by contact with some other material?

(ii) Can any steps be taken to protect skins from this weevil at any stage of production in India and in the course of shipment?

A.: The infestation of E. I. tanned skins, dry salted and dried sheep and goat skins by beetles can occur on the steamer in transit. The usual source of infestation is from the bones carried in the ships.

Dried or dry salted skins may be infested even prior to loading whereas tanned skins are not likely to be infested prior to being loaded into ships. It may be pointed out that in addition to the adult and larval forms of the hide beetle *Dermestes maculatus* (syn. *Dermestes vulpinus*), the prepupal larval stages migrate into harder materials like bales of leather prior to pupation, causing tunnels. The usual site of damage is in the fold along the backbone in the best part of the skins.

The possible ways of preventing such damage are: (i) avoiding ships carrying bones if possible; if not, the skins should be stored as far away as possible from the bones; (ii) treatment with insecticide: the bundles of skins may be dusted with dieldrin, aldrin or gammexane dusts (commercial quality) on the sides and burlap at the time of bundling. The gunny cloth used for bundling the hides may be soaked in wettable formulations of the above insecticides and dried before using for packing. Naphthalene also may be used in the same way for dry salted goat skins exported by ships.

CLASSIFIED ABSTRACTS

RAW MATERIALS

Variation in birth weight of Bihar and Bikaneri sheep and their crosses.

O N. Singh and J. N. Prasad (Animal Genetics Section, Livestock Research Station, Bihar, Patna) *The Indian Veterinary Journal* 39, 59 (1962). Studies have been made to investigate the birth weight of plain type Bihar sheep, Bikaneri sheep and their crosses, to determine the influence of varying degrees of Bikaneri inheritance on birth weight. In this present work, data were collected from the breeding project on grading up of Bihar sheep with Bikaneri rams and also on selective breeding of Bihar sheep and Bikaneri sheep carried out at Sheep Breeding Farm, Gaya (Bihar).

The mean birth weight of 228 lambs of different types of sheep under study was 5.19 ± 0.07 pounds, the weight of the male lambs, on the average, being more than that of the female lambs. It was noticed that birth weight was characteristic of breed or type of sheep. Plain region type sheep of Bihar had the lowest average birth weight, whereas the remaining three types of sheep were heavier than the mean weight of lambs of Bihar sheep. The effect of sex on birth weight was also found to be highly significant and this difference existed in plain type Bihar sheep and the Bikaneri sheep, the interaction of sex and breed having no significant effect on birth weight of lambs.

While considering the distribution of lambs in relation to their birth weights, it was observed that the larger percent of births in Bihar sheep fell under lower birth weight groups whereas it was reverse for the births in Bikaneri sheep and their crosses. Estimates of heritability for birth weight were made in the present study with sex and types of sheep. These estimates for male lambs were 0.073, 0.145 and 0.234 whereas for female lambs they were 0.016, 0.335 and 0.296 for Bihar sheep, Bikaneri and Graded Bikaneri sheep respectively. There appeared to be sex difference in heritability with little high positive values for female lambs.

K. C. S.

Studies on mineral and protein metabolism in goats in relation to the level of carotene feeding.

B. N. Majumdar (Post-graduate College of Animal Sciences, Indian Veterinary Research Institute, Izatnagar, U.P.) *Ann. Biochem. Exptl. Med.* **21**, 271 (1961). Carotene supplementation has been found to restore the appetite and increase the retention of protein, calcium and phosphorus in vitamin A-deficient goats. The significance of these findings has been discussed in relation to the possible metabolic role of vitamin A.

Effects of air temperature and humidity on the metabolism of nutrients in the buffalo.

G. V. Raghavan and D. N. Mullick (Animal Nutrition Division, Indian Veterinary Research Institute, Izatnagar, U.P.) *Ann. Biochem. Exptl. Med.* **21**, 277 (1961). The influence of seasonal variation on the metabolic behaviour of different nutrients was studied in the buffalo. The following findings have been reported: The amount of water intake, insensible perspiration and the ratio between the intake of water and dry matter showed a significant positive correlation with increase in the air temperature. The water outgo through urine and faeces and dry matter intake remained unaltered during these observations. The ingestion of protein and fat and their coefficients of digestion were higher in winter months whereas the reverse was the case with carbohydrate. The balances of nitrogen and phosphorus were maximum during winter whereas, the calcium balance did not show seasonal variation. Differences in the intake of water and proximate principles at different seasons were statistically significant. Under tropical conditions, the necessity of providing roughage of better nutritional value, such as hay or silage instead of cereal straws has been stressed.

VEGETABLE TANNAGE

A new method for the synthesis of Cis-Catechins.

M. D. Kashikar, R. S. Kulkarni, (Miss) A. M. Borkar and A. B. Kulkarni (Dept. of Chem. Inst. of Sci., Bombay 1) *Chem. and Ind.* **46**, 1892 (1961). Synthesis of a catechin by the reduction of flavanol benzoate with lithium aluminium hydride and subsequent hydrogenation of the complex *in situ* over Raney nickel has been reported earlier by the authors. It is now found that substitution of flavanol benzoate by the corresponding benzyl ether (mp. 114/45°C) in the reduction gives better yield of the catechin. The

method has been extended to syntheses of ($\pm$)-cis-afzelechin trimethyl ether, ($\pm$)-cis-fisetinidol trimethyl ether and ($\pm$)-cis-robinetinidol tetramethyl ether.

K. G. S.

CHROME TANNAGE

Polarographic studies on the combination between chromic chloride and collagen protein. II. Polarography on the aquo-chromic chloride.

Hiroshi Nunoura (Bioch. Lab. Faculty of Home Economics, Kyoto Women's Univ.) *Bull. Jap. Assoc. Leath. Tech.* **7**, No. 3, 75 (1962). (1) As $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{+++}$ were reduced at half wave potential of $-0.610\text{V. vs. S.C.E.}$ and $-0.910\text{V. vs. S.C.E.}$, it is possible to follow quantitatively the combined $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{+++}$ with hide powder. (2) The combined $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{+++}$ with hide powder increased as pH rose and this tendency was more with $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ than with $[\text{Cr}(\text{H}_2\text{O})_6]^{+++}$. In other words, $[\text{Cr}(\text{H}_2\text{O})_6]^{+++}$ is more stable than $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$. (3) It is expected that by polarographic methods the first reactions of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{+++}$ with hide powder are made clear.

Studies on ion distribution of $\text{Cr}(\text{OH})\text{SO}_4$ liquor added neutral salts.

K. Wada, T. Deshimaru and A. Kawamura (Tokyo University of Agriculture and Technology) *Bull. Jap. Assoc. Leath. Tech.* **7**, No. 3, 79 (1962). The relations between the paper electrochromatograms and the tanning potencies of the chrome liquors which were made by the addition of various neutral salts to $\text{Cr}(\text{OH})\text{SO}_4$ liquor were studied. Prior to the experiment, the attitude of the salt free standard $\text{Cr}(\text{OH})\text{SO}_4$ on the electrical treatment was studied. The paper electrogram of $\text{Cr}(\text{OH})\text{SO}_4$ is composed of five cationic parts ((a)~(e)), which can be determined by densitometer as five peaks, and the peaks of (a), (c), (d) are found to be the compounds which correspond to $[\text{Cr}]^{3+}$, $[\text{Cr}]^{2+}$ and $[\text{Cr}]^{1+}$. When the standard $\text{Cr}(\text{OH})\text{SO}_4$ liquor is heated at 100° for one hour, these peaks change their forms but can almost recover to the original states after ageing for one week. Moreover, because of the reason that the above standard curve does not change the form either when the liquor is diluted or when the time of the electrical treatment is prolonged, each compound in

$\text{Cr}(\text{OH})\text{SO}_4$ can be considered not so unstable at least in the unisolated state.

After adding various neutral salts (3eq/Cr) to the standard $\text{Cr}(\text{OH})\text{SO}_4$ solution and heating for one hour, the changes on the electrochromatograms were investigated by the densitometer and the results compared with their tanning potencies. By the experiments, neutral salts can be divided into three groups. The first group shows high tanning activity ($T_s > 90^\circ$), when mixing the salt with the standard $\text{Cr}(\text{OH})\text{SO}_4$ liquor: NaCl , Na_2SO_4 belong to this group. The characteristics of these chromium complexes shown on the densitometer indicate the (a), (c), (d) peaks clearly. Moreover, the height of (a) peak in this group is increased by the ageing. The second group shows rather low tanning potency ($T_s 80^\circ \sim 90^\circ$): Formate, succinate, adipate belong to this group. The characteristic of the chromium complexes of this group on the densitometer is that the (a) peak which cannot be seen immediately after heating appears gradually and each curve is transferred to the right side by the ageing. The last one group has the lowest tanning potency; acetate, lactate, tartrate and citrate belong to the group. The chromium complexes of the last group are composed of chiefly anionic, uncharged and highly coordinated ones.

OTHER TANNAGES

Studies on iron tanning. VI. The reversibility of the ferric sulphate tanning and the presumption of their adsorption mechanism.

Hide Nihiro (Bioch. Lab. Depart. of Home Economics, Kyoto Women's Univ.) *Bull. Jap. Assoc. Leath. Tech.* 7, No. 2, 29 (1961). The author investigated the mechanism of the fixation of iron complexes in the ferric sulphate or chloride tannage and the deironing from tanned leather. The results are as follows: (1) This iron tanning is completely a reversible reaction. The fixed iron complexes are easily removed by reducing the overall basicity of tanning system or by immersing the leather in the dilute mineral acid solution. These tanning and detanning can be effected without denaturation of the hide substance. (2) The leather tanned with ferric sulphate was neutralized or washed for reducing the amount of acid radicals in leather, and retanned with basic ferric sulphate solution. Then fresh iron fixation occurred and the amount of iron fixed by retanning was correlated to the acid binding capacity of leather. The maximum amount of iron obtained by repeating this treatment was 43.1% Fe_2O_3 on the hide substance.

But SO_4 content in leather was almost unaffected by this treatment. On the other hand, the amount of iron fixed from acidic iron liquor in which only a little of basic iron complexes existed and in which the fixation was due to the coordinated bond between the active groups of collagen and the iron complexes, was only 2-3% Fe_2O_3 on the hide substance. These results indicate that the tannage with basic ferric sulphate or chloride depends largely on the deposition of ferric hydroxide or basic iron complexes on collagen fibre and that it involves some chemical combination between collagen and the iron complexes.

Studies on iron tanning. VII. Melamine-formaldehyde after-treatments of iron-citrate tanned leather.

Hideo Nihiro (Bioch. Lab. Depart. of Home Economics, Kyoto women's Univ.) *Bull. Jap. Assoc. Leath. Tech.* 7, No. 2, 35 (1961). When the iron-citrate tanned leather was immersed in the dilute acid or alkali solution the pH value of the leather being at the region of 2.5-3.5, the T_s of this leather decreased drastically and the detanning occurred. This is the main defect of iron-citrate tanned leather. In comparing the improvements of chemical resistances of iron-citrate leather by the after-treatment with a number of chemicals, it has been found that the melamine-formaldehyde after treatment was most effective. Then the basic conditions of melamine-formaldehyde after-treatment were investigated and the following results obtained: (1) For the fixation of resin and the improvement of the leather properties, mono- and di-methylol melamine were more suitable than tri- or more methylol compounds. Therefore the treatment of the leather directly with mixing solution of melamine and formaline is better than the treatment with the preformed methylol melamine. In this case the methylolation of melamine and the condensation of methylol compounds occurred simultaneously and the free amide groups of melamine remained in the fixed resin. (2) The optimum condition of the treatment is that the pH of the solution is 3.3-4.5, the temperature is above 20° , the amount of melamine to the leather is 10-20% and the molar ratio of formaldehyde/melamine is 5-8. (3) The defect of melamine-formaldehyde after-treatment was that the methylol groups of melamine remained in the fixed resin and later condensed in storing and caused the hardening of the leather. It was found that these defects were removed easily by the esterification of methyl groups with the after-treatment of methyl alcohol. (4) Melamine-formaldehyde after-treatment increased T_s of iron citrate

tanned leather, and the maximum T_g of the treated leather in these experiments was 98°C. This treatment increased the fullness of the leather, but the water vapour permeability was almost unaffected.

PROCESSES AFTER TANNING

Upgrading leather with aqueous impregnants.

Peter R. Beuchler, *Leather Manufacturer*, 78, No. 2, 19 (1962). Treating leathers with aqueous solutions of polymers like acrylics produces in them some of the most desirable characteristics of synthetic products. First of all, the grain and corium are rather more firmly bonded so that on flexing a tight break is obtained. Secondly, because the polymer has a lot of "give" under impact together with good adhesion to the leather, it serves as a cushioning and supporting matrix, thus improving the scuff resistance. Thirdly, the rather loose belly and flanks are filled up, resulting in enhanced cutting value of the leathers.

Apart from this positive rectification of inherent defects many other advantages also accrue. For example, fewer number of finish coats have been found sufficient in finishing impregnated leathers. Secondly, if these finishes are plated at high temperatures, improved smoothness and lay-out are achieved. Thirdly, little or no retannage with vegetable tanning agents has been found necessary for leathers so impregnated. Finally, leathers impregnated with dyed acrylics acquire an increased light stability and level shade.

But all these should not be at the expense of the unique characteristics possessed by leather to preserve which, care must be taken. For example, to retain the ability to transmit moisture vapour, the impregnation must be partial leaving the entire corium free and as absorptive as before. Again, such a polymer as will transmit moisture vapour must be chosen. Secondly, in order to retain the characteristic leathery appearance, the polymer chosen should be one of low molecular weight. Also, it should not be one cross-linking on ageing. This is important because leathers impregnated with reactive polymers become brittle and crack as the polymer cures in course of time. Finally, since the leathers to be converted into shoe uppers are exposed to high temperatures and humidities and since they are pulled with great force over a last, it is necessary that the impregnated polymer should also swell and soften along with the leathers during these operations.

S. K.

TESTING

Spectrophotometric determination of ferric iron.

Giovanni Ceriotti and Luigi Spandrio (Centro Studio Tumori di Busto, Arsizio, Italy) *Anal. Chem.* 33, 579 (1961). Ferric iron oxidizes dimethyl-*p*-phenylenediamine giving a red pink colour proportional to the Fe(III) concentration ($\epsilon=9500$).

Determination of formaldehyde in gas mixtures by the chromotropic acid method.

Aubrey P. Altshuller, David L. Miller, and Stanley, F. Sleva (Division of Air Pollution, Robert A. Taft Sanitary Engg. Center, U.S. Depart. of Health, Education and Welfare, Cincinnati 26, Ohio) *Anal. Chem.* 33, 621 (1961). The modification of the chromotropic acid method for formaldehyde proposed by West and Sen has been investigated. With only minor variations, the present study confirms the previous findings on reagent concentrations, colour stability of the product, and the stability of the reagent solution. A much more detailed investigation of the possible interference of olefins, alcohols, aldehydes and ketones, aromatic hydrocarbons, phenols, and of nitrogen dioxide has been made. Nitrogen dioxide, most aldehydes and ketones, and straight-chain alcohols do not interfere significantly. The interference of olefins and aromatic hydrocarbons can be largely eliminated by the use of appropriate sampling conditions.

Microdetermination of formaldehyde in air.

A. C. Rayner and C. M. Jephcott (Air Pollution Control Branch, Ontario Dept. of Health, Toronto, Canada) *Anal. Chem.* 33, 627 (1961). A procedure is described for determining the concentration of formaldehyde in air. Formaldehyde is collected by drawing air at a rate of 1 c.f.m. through an impinger containing 0.005 *N* hydrochloric acid. The collecting efficiency of this solution is 72% with a standard deviation of 5%. A magenta colour is produced by adding Schiff's reagent to the formaldehyde solution; acetone increases the depth and stability of the colour. The absorbance is measured in a spectrophotometer at 560 m μ . The method is sensitive to 0.1 μ g. of formaldehyde per ml. of collecting solution. With a sampling period of 1 hour, a concentration as low as 5 p.p.b. in air can be determined. Typical results for urban air are presented. Diurnal variations in formaldehyde concentration are found, with peaks occurring during the morning and late afternoon.

The spectra of inorganic complexes in nonaqueous solvents. Part I. Chlorocobaltate ion and cobalt chloride.

S. Buffagni and T. M. Dunn, *J. Chem. Soc.* 5105 (1961). The spectra of CoCl_2 and the $(\text{CoCl}_4)^{2-}$ ion have been examined in various non-aqueous solvents, particularly nitromethane and NN-dimethyl-formamide. The results show that there is a considerable amount of interaction between the "solute" and the "solvent" and that species postulated as $(\text{CoCl}_2\text{S}_2)$, $(\text{CoCl}_3\text{S})^-$, $(\text{CoS}_6)^{2+}$, and $(\text{CoS}_5\text{Cl})^+$ occur in varying, but appreciable, amounts.

Protein fractionation. IV. Characterization of serum lipoproteins by chromatography on DEAE-cellulose.

Morton D. Prager and Ina Claire Atkins (Wadley Research Institute and Blood Bank, Dallas, Texas, U.S.A.) *Biochem. Biophys. Acta.* 54, 405 (1961). Chromatography on DEAE-cellulose was performed with sera from patients with polycythemia vera and granulocytic leukemia, who were treated with ionic ^{32}P . Four ^{32}P peaks are consistently found in these chromatograms, following introduction of buffers II, IV, V, and VII, numbered in the order of increasing phosphate concentration and decreasing pH; an additional peak was noted following buffer VI for two of the sera. Partition of the ^{32}P between aqueous and lipid solvents showed greater than 90% of the activity to be in the lipid phase except for peak II. The latter also was dialyzable and was identified as inorganic PO_4 . The principal phosphatide associated with peaks IV, V, VI and VII was identified as lecithin by paper chromatography and infrared analysis. Low density lipoproteins which float at $79674 \times g$ in a medium of specific gravity 1.063 were found in ^{32}P peak VII. The lipoproteins of peaks IV and V were high-density lipoproteins (density > 1.063); in correlation with this identification, the electrophoretic mobility of IV was that of α -lipoprotein.

THEORIES

Connective tissue development in subcutaneously implanted polyvinyl sponge. I. Biochemical changes during development.

J. F. Woessner, Jr. and Robert J. Boucek (Howard Hughes Medical Institute, Miami, Florida, U.S.A.) *Arch. Biochem. Biophys.* 93, 85 (1961). The changes in wet weight, soluble protein, deoxyribonucleic acid (DNA), collagen, free hydroxyproline, and ascorbic acid have been measured during the process of connective tissue development in polyvinyl sponge implants in the female

rat. There was a continual decrease in tissue wet weight during the first 20 days after sponge implantation, accompanied by a reduction in the sponge volume. The amount of soluble proteins per gram of implanted sponge remained constant throughout the period of development. Deoxyribonucleic acid increased to a maximum at 20 days and then remained relatively constant. Ascorbic acid was present initially in high concentration in the extracellular fluid and underwent further increases in parallel with DNA. Collagen accumulation reached a maximum by 36 days. Free hydroxyproline paralleled the appearance of DNA. No relationship could be established between free hydroxyproline and collagen synthesis or degradation.

Connective tissue development in subcutaneously implanted polyvinyl sponge. II. Enzymic changes during development.

J. F. Woessner, Jr. and Robert J. Boucek (Howard Hughes Medical Institute, Miami, Florida) *Arch. Biochem. Biophys.* 93, 95 (1961). The changes in enzyme activity that accompany connective tissue development in polyvinyl sponge implants in female rats have been measured quantitatively. The enzyme activities are grouped into three general developmental patterns, which are related to processes of cell proliferation, tissue maturation, and collagen synthesis and degradation. Glutamic oxalacetic transaminase, imidodipeptidase, iminodipeptidase, catalase, cytochrome c reductase and phenolsulfatase activities develop in parallel with deoxyribonucleic acid (DNA) and then remain at a relatively constant level during the remainder of tissue development. Proteinase (pH 3.2), acid phosphatase, and β -glucuronidase activities continue to increase when the DNA and collagen content have reached their maximum levels. Alkaline phosphatase, peroxidase, lactic dehydrogenase, and malic dehydrogenase activities pass through a maximum and then decline before, or at the same time, DNA reaches its maximum.

The interaction of a nonionic detergent with protein. I. Physical properties of the protein detergent complex.

Robert M. Dowben and Walter R. Koehler (Depart. of Med., Northwestern Univ., Chicago, Illinois and the Medical Res. Labs., Veterans Administration Res. Hospital, Chicago, Illinois, U.S.A.), *Arch. Biochem. Biophys.* 93, 496 (1961). The addition of Triton X-100, a nonionic detergent, to solutions of bovine plasma albumin resulted in a small but significant increase in intrinsic viscosity and a decrease in electrophoretic mobility. The specific optical

rotation of bovine plasma albumin, ribonuclease, and oxidized ribonuclease was unchanged by the addition of detergent. The number of reactive sulfhydryl groups of bovine serum albumin and muscle aldolase was unchanged in the presence of detergent. These data indicate that no gross structural change occurs in the protein but are consistent with the view that the degree of hydration is increased in the presence of detergent.

GENERAL

Fungal detoxication. Part V. Metabolism of *o*- and *p*-chlorophenoxyacetic acids by *Aspergillus niger*.

J. K. Faulkner and D. Woodcock, *J. Chem. Soc.* 5397 (1961). In the metabolism of *p*-chlorophenoxyacetic acid by *Aspergillus niger* (replacement culture technique), 4-chloro-3-hydroxyphenoxyacetic acid, hitherto unknown, is formed in addition to the corresponding 2-hydroxy-acid. When *o*-chlorophenoxyacetic acid is the sole carbon source, hydroxylation takes place at all vacant ring positions, the main products being 2-chloro-4-hydroxyphenoxyacetic acid, together with 2-chloro-5-hydroxyphenoxyacetic acid. The corresponding 3- and 6-hydroxy-compounds are produced in much smaller amounts, and the additional formation of *o*-hydroxyphenoxyacetic acid appears to be the first example of fungal replacement of chlorine by hydroxyl.

Composition of beeswax. Part I. Fractionation of beeswax and its alcohols with urea.

T. N. Mehta and B. N. Murthy (Laxminarayan Institute of Technology, Nagpur University) *Indian J. Appl. Chem.* 24, 153 (1961). Beeswax obtained locally (I.V. 7·60, Sap. 97·8, A.V. 6·13 and H.V. 16·51) was saponified, and the alcohols separated from the hydrocarbons and unsaponifiable portion, were acetylated. The acetates were fractionated with urea for finding the fatty alcohol composition which is as follows: C₂₆ 8·2, C₂₈ 30·4, C₃₀ 52·0, C₃₂ 7·4 and cyclic and branched alcohols 2·1%. Fractionation of beeswax with urea suggests a useful method for deriving hard and soft varieties of the wax required in the manufacture of cosmetics, candles and other products.

Composition of beeswax. Part II. Fractionation of fatty acids.

T. N. Mehta and B. N. Murthy (Laxminarayan Institute of Technology, Nagpur University, Nagpur), *Indian J. Appl. Chem.* 24, 158 (1961). The fatty acids of beeswax were resolved into

three groups by extraction with aqueous alcohol. The ethyl esters of these acids were fractionated with urea to arrive at the fatty acid composition which is as follows: Hydroxy acids 20·24%, unsaturated acids 9·84% and saturated acids 69·92%. C₁₆ and C₁₈ acids were found to be the most predominant among the saturated acids. Fractionation of ethyl esters of the mixed acid of beeswax with aqueous 55% ethanol indicates the proportion of hydroxy and unsaturated acids to be 22·15% and 9·11% respectively.

Further studies on the pancreatic hydrolysis of some natural fats.

M. H. Coleman (Unilever Research Laboratory, Colworth House, Sharnbrook, Bedford, England) *J. Am. Oil Chemists' Soc.* 38, 685 (1961). A series of animal and vegetable fats has been subjected to hydrolysis with pancreatic lipase. From the results obtained, the triglyceride compositions of the original fats have been calculated by the method previously proposed by Coleman and Fulton. These compositions show substantial agreement with those obtained by other methods. Similarities and differences between fats are shown to be reflections of similarities and differences in glyceride composition. The middle position of the triglycerides has been shown to be largely occupied by unsaturated acids in the case of shea, illipe, and cocoa butters; and by palmitic acid in the case of lard. From a study of the glyceride compositions of a series of lards, of differing fatty acid content, it is suggested that the glyceride composition of a lard may be predicted from a knowledge of its fatty acid content alone. It is concluded that the hydrolysis procedure, and the method of interpreting the results proposed together provide a simple and rapid method for the analysis of natural fats.

The possibility of reducing the work content of leather in manufacturing processes.

Keith M. Roper, *J. Soc. Leather Trades' Chemists*, 46, 3, (1962). This essay which was awarded the Donald Burton Prize for 1961, describes the main ways to increase productivity of labour in the tannery through large scale automation. There is, indeed, much scope in the leather manufacturing processes for a tangible decrease in the production costs by reducing the direct labour. A great deal of manual labour employed in moving leather from process to process and in operating machinery, which amounts to an increase in the cost of leather production, can be effectively controlled by adoption of most economical working procedures.

Good forward planning of production and organisation of processing along special production lines can lead in large tanneries to better standardised production at lower cost. The 'work content' of the leather can be reduced by application of 'work study' to tannery processes, leading to a better utilisation of existing plant and man-power. 'Method study' which involves detailed factual recording of working techniques is much helpful to identify and eliminate unproductive work. Thus it spotlights the shortcomings of production methods and promotes introduction of new systems of working. Any movement towards automation in tannery will necessitate fundamental changes in processing.

The effectiveness of employees can be increased by creation of some of the most powerful incentives such as incentive payment schemes etc. A more economic production can also be established in the case of large tanneries by discouraging manufacture of a variety of leathers and by concentrating only on a limited number of lines for which there is particular demand. Thus there are advantages as the sequence of manufacture becomes firmly established and the labour force increases the efficiency by the same pattern of working.

While considering the improvements to the existing or 'new type' machines, emphasis must be laid on the linking together of the different phases of manufacture by mechanical means.

Adequate research into new techniques is needed to ensure success in this field. The future of leather industry undoubtedly depends on how best this industry can meet the challenges from the competitive industries. The role of continued application of research to the industry is of much importance in this regard, for achieving the maximum efficiency of labour force successfully.

K. C. S.

NOTES AND NEWS

U.S.S.R. Imports of hides up substantially in 1961

The U.S.S.R. is an important importer of what it calls "leather raw materials". These imports rose from a value of 39,869,000 roubles in 1959 to one of 47,486,000 roubles last year. That included 3,100,000 (2,800,000) large hides worth 25,536,000 (22,497,000) roubles and 19,900,000 (18,800,000) small hides worth 21,923,000 (17,316,000) roubles.

Tanned leather imports fell sharply over the same period, however, from a value of 7,994,000 roubles to one of only 4,996,000 roubles. These imports included 1,200 (2,500) tons of sole leather worth 1,144,000 (2,109,000) roubles and 60,900,000 (84,000,000) square metres of upper leather worth 3,852,000 (5,885,000) roubles.

Leather shoe output in the first half of 1961 rose by 5% over the corresponding period of last year to 220,000,000 pairs. Total production in 1960 was 418,000,000 pairs, against 380,000,000 in 1959.

Polish Trade:

In the case of the Cominform satellite countries of Eastern Europe there was a slight fall in the value of the total output of the Polish leather, fur and footwear industry from 6,076,500,000 zloty to 6,030,300,000 zloty in the first half of 1961.

A reduction in imports of raw cattle hides from 16,776 tons green weight to 15,075 tons green weight resulted in Poland's output of hard leather falling from 11,619 tons to 10,207 tons in the first half of 1961. Soft leather production rose slightly during 1961 from 6,801,000 square metres for January-June, 1960, to 6,848,000 square metres for January-June, 1961.

A drop in hard leather output is also reported in annual official statistics covering the East German zone. This fell from 12,841 tons, in 1959, to 12,175 tons last year. Although the trade position in East Germany appears to be rather better than that in Poland for the first half of 1961, East Germany also bought fewer raw hides than in the corresponding previous period. Imports fell from

22,174 tons green weight in 1959, to 20,033 tons in 1960; while imports of soft leather rose from 105,100 square metres to 121,000 metres over the year. This was accompanied by a rise in domestic soft leather output from 9,470,000 square metres to 10,221,000 square metres.

A more cheerful picture is provided by the Hungarian leather industry. In Hungary, output of upper leather rose by 10% to 2,345,000 square metres in the first nine months of 1961 as compared with January-September, 1960. Sole butts production was maintained at the previous period's level of some 7,218 tons. Leather footwear output increased, too, over the period under review by 10% to 17,245,000 pairs. Exports increased by as much as 34% to 4,802,000 pairs.

Bulgarian Government statistics show that, in the first half of 1961 national output was only 1,842 tons of hard leather and 86,000,000 square metres of upper leathers, as compared with totals for the first six months of 1960 of 2,528 tons and 98,200,000 square metres respectively. Soft leather output rose from 51,400,000 square metres to 57,900,000 square metres over the period, while leather shoe production increased slightly from 2,240,000 to 2,303,000 pairs.

In Romania:

In the first half of 1961 the production index of the Romanian leather goods, fur and footwear industry reached the record level of 1962, taking 1955 as 100. Nevertheless, 1960, as a full year, saw a falling-off in raw hide imports from 8,700 tons to only 5,200 tons. This was in line with the general drop in hide sales to other Eastern European countries.

Like these countries, too, Romania is interested in building-up leather footwear exports, which increased in 1960 by more than 87% compared with 1959. This was achieved despite a much slighter increase in actual production. Romanian effort to push export sales of finished leather is noticeable. The trading organisation responsible is now offering an expanded catalogue.

Current Czech figures show an increase in cow hide leather imports in January-June, 1961, of some 20,000 tons, as against 17,000 tons imported over the corresponding period in 1960. Czechoslovakia, also, is building up shoe exports. She sold some 9,976,000 pairs of leather shoes abroad in the first half of 1961 as against export sales of 9,042,000 pairs for January-June, 1960.

Little is known about Albanian production and trade except that hides and skins play a relatively important part in its export economy and that it regularly sells quantities to other Eastern European and certain other countries. Last annual statistics available show an annual production of some 34,000 square metres of red leather, 61,000 square metres of calfskin and kidskin, 34,000 square metres of other area-measured leather, 99 tons of sole leather and 148 tons of strip leather.

Leather Trades Review: January 10, 1962.

Madras tanned hide and skin exports in 1961

A total of 40,384 bales of tanned E.I. hides and 28,327 of E.I. tanned skins were exported from Madras during 1961.

These totals comprised of exports to the following destinations: to U.K.: 29,445 cow, 356 buffalo, 2,629 cow calf, 3,673 buff calf, 3,889 sheep, 5,791 goat. To the Continent: 155 cow, 14 buffalo, 663 cow calf, 390 buff calf, 4,193 sheep, 9,762 goat.

To Japan: 2,215 sheep, 50 goat. To U.S.A.: 4 cow, 1,290 buffalo, 11 cow calf, 1,754 buff calf, 23 sheep, 2,033 goat. To Australia: 169 sheep and 202 goat.

Leather Trades Review: January 10, 1962.

Sheepskins are now useful nursing aid in Australia

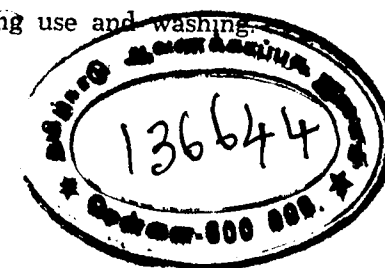
Ten months' experience in the wards of the Alfred Hospital, Melbourne, Victoria, Australia, suggests that nursing patients on sheepskins adds materially to their comfort. Laundering is not difficult and the skins seem to stand up well to constant use and frequent washing, according to a report in *The Lancet*.

Merino and merino cross skins were found to be suitable and with the following characteristics:

Soft wool and dense fleece: fibre diameters of 22 μ -28 μ corresponding to the range 56s.-64s. quality, provide the required softness and density.

Springy or resilient wool which recovers quickly from the depressed state.

Fibres which do not cot or mat during use and washing.



The skins used have an average size of 8 sq. ft., and are chrome-tanned so that they will withstand high temperature and washing without shrinking. The skin is spread on top of the sheet, wool side up, and patients are persuaded, if possible, to lie directly on them. Since the wool fibres allow free circulation of air, absorb moisture up to 33% of their dry weight without feeling wet, and dissipate moisture readily, the three chief causes of bed sores—pressure, friction and moisture—are considerably reduced.

The skins have also been tried in two units in a large public hospital. Sheepskins have also been in use in the Druid General Hospital at Tuscaloosa, Alabama, for some years, the report adds, and their value is increasingly recognised in North America. In the U.K., trials are now taking place.

Leather Trades Review: January 17, 1962.

French leather exports to Common Market

Quantitative restrictions on exports of hides and skins to other Common Market countries will shortly be abolished by the French Government, according to the French Leather Council.

At present, the export of calfskins and horse hides is subject to an export quota scheme. This will be revised for countries belonging to E.E.C. as a result of the passing to the second stage of the Common Market.

According to the Leather Council, a number of traditional formalities would remain, in particular the handling of the sales under licence but there would be no quantitative limitation to them.

The other Common Market countries committed themselves not to reexport French hides and skins outside the Community.

For countries outside the Common Market, the existing restrictions will be maintained. An announcement on the new steps is expected to be made by the French Government before the end of January.

Leather Trades Review: January 31, 1962.

E.E.C. ban on certain reexports

The Executive Commission of the Common Market has recommended a ban on reexports from Luxemburg of certain raw hides

and skins to third countries. The ban should apply as follows (country of origin in parentheses):

Heavy cattle hides or parts, apart from inferior pieces (West Germany, France); light cattle hides, or parts, apart from inferior pieces (West Germany, France, Italy); Calfskins and horse hides (West Germany, Benelux, France, Italy); Goatskins and sheepskins (France, Italy); Lambskins and kidskins (France, Italy); Rabbitskins (Italy).

The Commission is to review the situation again at the end of June to see what further action is necessary.

Leather Trades Review: February 14, 1962.

Exports of Indian goatskins to U.S.A. in 1960

United States imports of goatskins in 1960 amounted to 30.5 million lb. valued \$ 22.9 million. Compared to the preceding year, imports were 19% lower in terms of quantity and 13.5% in value. The following figures show the quantity and value of imports during 1959 and 1960.

	U.S. imports of goatskins from India (Figures in thousands)			
	1959		1960	
	lb.	\$	lb.	\$
Dry/Dry salted	33,163	23,540	26,254	19,797
Vegetable tanned	964	1,225	797	1,321
Green pickled	3,762	1,738	3,403	1,819
Total :	37,889	26,503	30,454	22,937

It will be observed from the above data that the largest decline both in quantity and value occurred in the case of imports of dry/dry salted goatskins, the respective figures being 20 and 15% over 1959. It is, however, noteworthy that while imports of vegetable tanned skins declined by 17% in quantity, there was an increase of 7% in value. Likewise, the value of imports of green pickled skins suffered a fall of 9% but the value figure was 4.5% higher than in 1959.

The shortfall in the volume of total U.S. imports from all countries also affected imports from India though in a varying degree. Imports by quantity were down by 28% but by value only 4% as compared with 1959. The following table shows the breakdown of imports from India during 1959 and 1960.

	U.S. imports of goatskins from India (Figures in thousands)			
	1959		1960	
	lb.	\$	lb.	\$
Dry/Dry salted	7,108	4,432	5,259	4,283
Vegetable tanned	937	1,180	696	1,137
Green pickled	2,312	994	1,473	786
Total :	10,357	6,606	7,428	6,206

The largest decline occurred in respect of imports of green pickled skins from India and was 36% in quantity and 20% in value. The fall in the value of imports of both dry/dry salted and vegetable tanned varieties was much less pronounced, being only 3% and 3.5% respectively as against 26 and 25% in quantity, than in dollar value which would show that Indian skins realized better prices during the year under review.

U.S. imports of goatskins from the principal supplying countries were as follows:

	U.S. imports of goatskins from India (Figures in thousands)			
	1959		1960	
	lb.	\$	lb.	\$
<i>Dry/Dry Salted :</i>				
Peru	1,694	725	1,786	790
Brazil	4,420	3,765	2,481	2,215
India	7,108	4,432	5,259	4,283
Pakistan	4,273	2,813	5,614	4,110
Nigeria	3,298	3,393	3,618	3,514
Ethiopia	3,749	3,056	1,229	984
Br. East Africa	2,266	1,805	1,708	1,242
Total (incl. imports from other countries)	33,163	23,540	26,254	19,797
<i>Green Pickled:</i>				
Iran	1,372	710	1,348	775
India	2,312	994	1,473	786
Total (incl. imports from other countries)	3,762	1,738	3,403	1,819

Vegetable tanned:

India	937	1,180	696	1,137
Total (incl. imports from other countries)	964	1,225	797	1,321

India's share in import trade of all the three types of goat-skins declined in terms of quantity from 27.3% in 1959 to 24.3% in 1960, but increased by about 3% in terms of value.

Export Promotion:

India has not yet explored the import market in U.S.A. for various types of hides and skins. India has three different types of hides and skins in abundance. The following figures show U.S. imports in 1960 of hides and skins of cattle, calf, buffalo, sheep and reptile skins. Also shown are imports of these from India in 1960. As will be seen, India's percentage share is only 1.08% in quantity and 2.08% in value.

	U.S. imports of goatskins from India (Figures in thousands)			
	From all others 1959		From India 1960	
	lb.	\$	lb.	\$
<i>Type:</i>				
Cattle hides dry	626	120	—	—
Cattle hides wet	14,489	2,375	—	—
Calf hide dry	6,179	3,104	90	58
Buffalo hides	1,533	884	1,192	677
Water buffalo hides	237	93	6	4
<i>Sheep and lamb skins:</i>				
(a) Shearlings	891	605	—	—
(b) Stats, dry, no wool	925	469	2	4
(c) Pickled not split	55,416	24,262	86	58
(d) Pickled split	725	416	—	—
Reptile skins	1,278	2,761	148	204
Total :	82,299	35,089	1,524	1,005

Export Promotion Bulletin, Madras: January 28, 1962.

10% rise in world hides, skins output in 1961

The output of hides and skins in the principal producer countries was appreciably higher in 1961 and international trade in

cattle hides rose by some 10 per cent, over 1960 according to the latest report of the Commonwealth Economic Committee.

United States and Argentina retained their dominance on export markets. They accounted for over half the world trade in cattle hides. United States surplus was more than 20,000 tons higher than the 1960 figure of 1,96,800 tons, although high prices and shortage of supplies cut back shipments in the second half of the year.

This year the slightly higher feed prices may tend to encourage the slaughter of cattle at somewhat lighter weights, but estimates of the size of the total United States herd suggest a further increase in killings.

Japan established itself as the largest single major importer in 1961, expanding its intake by about a half. But the European Economic Community which takes well over 50 per cent of the available supplies on world market remains firmly entrenched as a centre of trade in hides and skins.

The Economic Times: April 7, 1962.

Export of wool, animal meal

The Government of India has announced its policy in regard to the export of raw wool during the April to September, 1962 period.

A trade notice issued in this connection by the Joint Chief Controller of exports says that the export of raw wool will be allowed on contract and consignment basis against ceilings.

Licences will be issued on a first-come-first-served basis to all categories of shippers on shipping bills submitted with an application in the prescribed form and subject to the condition that certificates of Agmark grading are produced to the Customs authorities by the exporter at the time of shipment.

In the case of consignment basis, the announcement says that no shipper will be permitted to export more than 100 bales from all ports taken together.

Shipping bills will be made valid only for 15 days.

Horn and hoof meal, sterilised animal meal, blood meal, meat meal and fish manure will continue to be licensed freely for export

to all permissible destinations till March 31, 1963, the Joint Chief Controller of Exports announced.

The Economic Times: April 11, 1962.

Footwear output in Third Plan will rise by 40%

A 40 per cent increase in the output of leather footwear is expected by the end of the Third Plan, according to official figures. It is anticipated that the present rate of production of 100 million pairs will reach the figure of 140 million pairs by 1965-66.

At present about 2.50 million pairs of leather footwear are exported every year, bringing to this country foreign exchange of the value of Rs. 2.50 crores. It is envisaged that by 1965-66 exports will increase to between 4 and 5 million pairs. Production is being stepped up during the Third Plan mainly by expanding activity in the unorganised cottage and small-scale sector of the industry, which turns out 90 per cent of the output. Only 10 per cent of the production is accounted for by the organised sector, in which there are 12 major factories.

The Development Council for Leather and Leather Goods Industries has estimated the country's requirements of leather footwear in 1965-66 at 140 million pairs, including the 4 to 5 million pairs expected to be exported. Five of the large factories producing footwear are located in Uttar Pradesh. One factory each is situated in West Bengal, Bihar, Maharashtra, Madhya Pradesh, Madras, Punjab and Mysore. The 12 factories together have an annual production capacity of over 7 million pairs of Western type footwear, besides an unestimated but considerable production capacity of Indian type footwear, which are made by hand.

In view of the fact that the leather footwear industry can be organised on a labour-intensive basis and considering the fact that a substantial expansion in employment opportunities is one of the main aims of the Third Plan, no expansion of capacity in the large-scale organised sector of the industry is envisaged during the Third Plan period by the planners. The additional demand for footwear is planned to be met by a fuller utilisation of the existing capacity in the large-scale organised sector of the industry and by developments in the cottage and small-scale sectors.

It is estimated that for achieving the target of 140 million pairs of footwear, the industry would require as raw material about 14.5 million tanned hides and 6.5 million tanned skins. This is expected to be available from indigenous production. Produc-

tion of tanned hides in the country in 1960-61 was about 19.5 million and of tanned skins about 28 million. It is anticipated that by the Third Plan end, production of tanned hides will increase to 22 million and that of tanned skins to 30 million.

The Economic Times: May 1, 1962.

Woollen industry development

Recommendations of Council

The first meeting of the reconstituted Development Council for Woollen Industry was held in Bombay under the chairmanship of Mr. R. K. Birla. The Council made the following recommendations:

A limited number of woollen spindles may be allowed to spin shoddy yarn provided they had the necessary equipment for doing so and no imports of additional machinery and accessories, are involved. Allocation of import quotas for raw material may be made in future on the basis of number of spindles installed, subject to some adjustment in respect of worsted spindles producing a larger percentage of hosiery and knitting yarn or weaving yarn. The pattern of production of different kinds of worsted yarns may be revised so as to ensure an adequate production of all weaving yarn, hosiery yarn and knitting yarn out of imported raw material.

Distribution of yarn

A committee consisting of Mr. R. K. Birla, Mr. T. N. Khaitan and Mr. Satish Chandra Mahajan be appointed, with powers to co-opt other members to arrange distribution of worsted, weaving, and knitting yarn on the same lines as is being done in the case of art silk yarn.

A Scheme for the utilisation of Indian wool for the manufacture of worsted yarn was approved. Individual mills be asked to submit plans for the rehabilitation and modernisation of their units. A suitable revision of the incentives available under the Export Promotion Scheme for woollen goods be made and at least 10 per cent of the incentives should be compulsorily earmarked for the import of machinery. The exporters may be allowed the same incentives as are available to the manufacturer-exporters.

There should be no quota restrictions for exports of raw wool to various countries nor should there be any ceiling on exports of individual exporters.

A seven-member committee, with Mr. Khaitan as Chairman was appointed to prepare a technical plan for the establishment of a research institute for the woollen industry with the assistance of the Council of Scientific and Industrial Research.

The Hindu: April 22, 1962.

Export of "Jootis" from Rajasthan

The "jootis"—light shoes—made in Rajasthan are becoming popular in foreign countries. Last year about ten thousand shoes of this type were exported. Latest census figures show that 62,000 persons are engaged in leather industry in Rajasthan. Till recently, hides were exported from the State with the result that workers engaged in this industry did not have sufficient work. A loan of over rupees four lakhs and a subsidy of about rupees six lakhs given by the Rajasthan Khadi Board to co-operative societies and individual workers engaged in leather industry last year have helped them to develop tanning and colouring of leather and production of various articles. Last year leather goods worth Rs. 93,000 were sold by the co-operative societies alone.

The Hindu: April 24, 1962.

Institution of Chemists (India)

Associateship Examination 1963

The Thirteenth Associateship Examination of the Institution of Chemists (India) will be held in November, 1963. The last date for Registration is 30th November, 1962. The Examination in Group A (Analytical Chemistry) is divided into the following eleven sections and each candidate will be examined in two of them according to his choice as approved by the Council, in addition to the General Chemistry including Organic, Inorganic, Physical and Applied Analytical-Chemistry: (1) Analysis of Minerals, Silicates, Ores and Alloys; (2) Analysis of Drugs and Pharmaceuticals; (3) Analysis of Foods; (4) Analysis of Water and Sewage; (5) Biochemical Analysis; (6) Analysis of Oils, Fats and Soaps; (7) Fuel and Gas Analysis; (8) Analysis of Soils and Fertilisers; (9) Analysis connected with Forensic Chemistry; (10) Analysis connected with Leather Chemistry and (11) Analysis connected with Textile Chemistry. The Examination is recognised by the Government of India as equivalent to M.Sc. in Chemistry for purposes of recruitment of Chemists.

Further enquiries may be made to the Honorary Secretaries, Institution of Chemists (India) Chemical Department, Medical College, Calcutta-12.

C.L.R.I. NEWS

Dr. Y. Nayudamma, Director, has been nominated as a member of the Governing Body of the Indian Standards Institution for a period of one year from 1-1-1962.

Dr. Y. Nayudamma, Director, attended the 28th meeting of the Governing Body of Madras Productivity Council held on April 21, 1962.

The Annual Day of the Staff Club, C.L.R.I. was celebrated on April 4, 1962 with Sri R. M. Mahadevan, Commissioner of Police, Madras as the Chief Guest. Mrs. Mahadevan distributed the prizes to the winners of various competitions held in connection with the Club Day Celebration. The members of the Club staged a delightful variety entertainment programme.



The lady members of C.L.R.I. staff who staged Mrs. Sarojini Naidu's "Queen's Rival"

சென்ட்ரல் லெதர் ரிசர்ச் இன்ஸ்டிடியூட் புல்லட்டின்

இணைப்பு ஏடு, மே, 1962

“பை” முறையில் பதனிடுதல்

அஷ்வான் பட்டையும் கடுக்காயையும் கலந்து
பை முறையில் பதனிடுதல்
(மேம்பாடு செய்யப்பட்ட முறை)

ஜி. என். ஹோர், ஏ. கணேசன்

கச்சாப் பொருள் :

ஒவ்வொன்றும் 50-55 ராத்தல் (22.7 - 24.9 கி. கிராம்)
எடை உள்ள எருமை உப்புத் தோல்கள்.

1-ம் நாள் : நனைவு

போதுமான அளவு தண்ணீர் நிரப்பப்பட்ட ஒரு குழியில் முதலில் இவை 5 நிமிடங்களுக்குக் கழுவப்படுகின்றன. பின்னர் மற்றொரு குழியில் சுத்தமான தண்ணீரில் 4 மணி நேரத்திற்கு நனைத்து வைக்கப்படுகின்றன. பின்னர் தோலிலுள்ள அழுக்கு முதலியவை போகுமாறு 5 நிமிடங்களுக்கு அரக்கிக் கழுவப்பட்டுப் பாளங்களாக்கப்படுகின்றன. பின்னர் இவை வடிய வைக்கப்பட்டு, நனைவு எடை குறித்துக் கொள்ளப்படுகிறது.

சுண்ணாம்பிடுதல் :

பின்வரும் அளவில் கீழ்க்கண்டவாறு ஒரு பூச்சு தயாரிக்கப்படுகிறது.

(கொடுக்கப்பட்ட அளவுகள் 100 ராத்தல் நனைவு எடைக்கு கணக்கிடப்பட்டவையாகும்)

சோடியம் சல்பைடு	1%
தாளித்த சுண்ணாம்பு	5½%
தண்ணீர்	15—20%

முதலில் சோடியம் சல்பைடு தூளாக்கப்பட்டு, குறைந்த அளவு கொதி நீர் கொண்ட பானையில் கரைக்கப்படுகிறது. பின்னர் இத்துடன் சுண்ணாம்பும் தண்ணீரும் கலக்கப்பட்டு, போதுமான அளவு கெட்டியான பூச்சு தயாரிக்கப்படுகிறது. இப்பூச்சு வடிய வைக்கப்பட்ட பாளங்களின் மேனிப்பக்கமும், சவ்வுப் பக்கமும் பூசப்படுகிறது. பின்னர் பாளங்கள் மடிக்கப்பட்டுப் பட்டறையாக விடப்பட்டு, கோணியால் மூடப்பட்டு, இரவு முழுதும் விட்டு வைக்கப்படுகின்றன.

2-ம் நாள் :

பாளங்கள் பட்டறையிலிருந்து எடுக்கப்பட்டு, ஏற்கனவே இரண்டு கட்டுத் தோல்களுக்கு உபயோகிக்கப்பட்ட பழைய சுண்ணாம்புத் தண்ணீரில் தள்ளப்பட்டு, காலை யில் ஒரு முறையும், மாலையில் ஒரு முறையும் குழி திருப்பப் படுகின்றன.

3-ம் நாள் :

குழி திருப்பப்படுகின்றன.

4-ம் நாள் :

வழக்கம் போல் இவை முடி தள்ளப்படுகின்றன. பின்னர் நனைவு எடையில் 400% தண்ணீரும் 5% தாளித்த சுண்ணாம்பும் கொண்டு தயாரிக்கப்பட்ட புதிய சுண்ணாம்புத் தண்ணீரில் போடப்பட்டு மாலையில் ஒரு தடவை குழி திருப்பப்படுகின்றன.

5, 6-ம் நாட்கள் :

குழி திருப்பப்படுகின்றன.

7-ம் நாள் :

பாளங்கள் சல்லா சீவப்படுகின்றன. சல்லா எடை குறித்துக் கொள்ளப்படுகிறது.

சுண்ணாம்பு நீக்கம் (இளங்காரம்) :

150% தண்ணீரில் 1% அமோனியம் சல்பேட் கலக்கப் பட்டு, இதில் தோல்கள் போடப்பட்டுச் சுண்ணாம்பு நீக்கம் (இளங்காரம்) செய்யப்படுகின்றன. பிறகு இரவு முழுதும் இத்திரவத்திலேயே விட்டு வைக்கப்படுகின்றன.

முதல் பட்டைத் தண்ணீர் தயாரித்தல் :

அஷ்வான் பட்டையும், தூள் கடுக்காயும் 3 : 1 என்ற விகிதத்தில் கலக்கப்படுகின்றன. இக்கலவை சல்லா எடையில் 150% எடுத்துக் கொள்ளப்படுகிறது. இதில் $\frac{1}{2}$ பாகம் போதிய தண்ணீர் நிரம்பிய குழியில் போடப்பட்டு, முதல் பட்டைத் தண்ணீர் தயாரிக்கப்படுகிறது. இங்ஙனம் தயாரிக்கப்பட்ட பட்டைத் தண்ணீர் மறுநாள் உபயோகத்துக் காக வைக்கப்படுகிறது. அஷ்வான் பட்டை—கடுக்காய் கலவையில் மீதியுள்ள $\frac{1}{2}$ பாகம் பை முறையில் பதனிடுவதற்கு உபயோகிக்கப்படுகிறது.

8-ம் நாள் :

கனமான தோலின் கனமான பகுதியிலிருந்து ஒரு சிறு துண்டு வெட்டி எடுக்கப்பட்டு, பிளாஸ்தீன் அல்லது மஞ்சள் உபயோகித்துச் சுண்ணாம்பு நீக்கம் பரிசோதிக்கப் படுகிறது. மேனிப் பக்கத்திலிருந்து $\frac{1}{3}$ பாகமும், சவ்வுப் பக்கத்திலிருந்து $\frac{1}{3}$ பாகமும் சுண்ணாம்பு நீங்கியிருந்தால் போதுமானது. பாளங்கள் பின்னர் கார் வாங்கப்பட்டு, இரண்டு தடவைகள் தண்ணீர் மாற்றிக் கழுவப்பட்டு முதல் பட்டைத் தண்ணீர் கொண்ட குழிக்கு எடுத்துச் செல்லப்படுகின்றன.

பாளங்கள் 10° வீர்யமுள்ள முதல் பட்டைத் தண்ணீர் கொண்ட குழியில் போடப்பட்டு காலை 2 மணி நேரமும் மாலையில் இரண்டு மணி நேரமும் புரட்டப்படுகின்றன. காற்றுக் குமிழிகள் ஏற்படாவண்ணமும், நிறப்போக்கு ஏற்படா வண்ணமும் எச்சரிக்கையாக இருக்க வேண்டும்.

9-ம் நாள் :

குழி திருப்பப்படுகின்றன.

10-ம் நாள் :

பாளங்கள் பை போல் தைக்கப்பட்டு குழிகளின் மேலே சட்டத்தில் கட்டித்தொங்கவிடப்படுகின்றன. அஷ்வான் பட்டை—கடுக்காய் கலவை இப்பைகளில் நிரப்பப்பட்டு, முந்தையக் கட்டுக்களைப் பதனிட்ட பிறகு மீதியிருக்கும் பட்டைத் தண்ணீர் பைகளில் ஊற்றப்படுகிறது. தேவையானால் கொஞ்சம் தண்ணீரையும் பைகளில் ஊற்றலாம். பைகளில் பட்டைத் தண்ணீர் காலியாக ஆக, கீழே உள்ள குழிகளிலிருந்து பட்டைத் தண்ணீரை எடுத்துப் பைகளில் நிரப்பிக்கொண்டே இருக்கவேண்டும்.

11-ம் நாள் :

பைகளில் பட்டைத் தண்ணீரை நிரப்பிப் பதனிடும் வேலை தொடர்ந்து செய்யப்படுகிறது.

12-ம் நாள் :

பைகள் தலைகீழாகத் தைக்கப்பட்டு பதனிடும் வேலை தொடர்ந்து செய்யப்படுகிறது.

13-ம் நாள் :

பைகளில் பட்டைத் தண்ணீரை நிரப்பிப் பதனிடும் வேலை தொடர்ந்து செய்யப்படுகிறது.

14-ம் நாள் :

பதனிடும் வேலை முடிவு பெறுகிறது. பைகள் பிரிக்கப் பட்டு, பைகளுக்குக் கீழே உள்ள குழிகளில் நாள் முழுதும் விட்டு வைக்கப்படுகின்றன.

15-ம் நாள் :

பாளங்கள் பிரஷ் அல்லது தேங்காய் நாரினால் நன்றாகத் தேய்த்துக் கழுவப்படுகின்றன. பின்னர் சல்லா எடையில் ½% சி. எல். ஆர். ஐ. 'பிளீச்சிங் சின்டான்' கொண்டு வெளுமையாக்கப்படுகின்றன. பிறகு தண்ணீரில் நன்றாக அலசப்பட்டு, வடிய வைக்கப்படுகின்றன. இதன் பின்னர் சல்லா எடையில் 2% கடலை எண்ணெய் பாளங்களின் மேல் பூசப்பட்டுக் காய வைப்பதற்காகத் தொங்கவிடப்படுகின்றன.

16-ம் நாள் :

பாளங்கள் சுருக்கம் (தாண) தள்ளப்பட்டு, முழுவதும் காய வைக்கப்படுகின்றன.

17-ம் நாள் :

பாளங்கள் நிறுக்கப்படுகின்றன. இம்முறையில் சல்லா எடையில் 55.3% பதனிடப்பட்ட தோல் கிடைத்தது.

(இம்முறை பீஹாரில் சன்தால் பர்கானா மாவட்டத்தில் சீதாக்காட்டு என்ற ஊரில் உள்ள பதனிடும் வோர் காலனியில் 1960-ம் ஆண்டு மே மாதத்தில் நேரில் செய்து காட்டப் பட்டது.)

செய்திக் கதிர்

கச்சா வெள்ளாட்டுத் தோல் ஏற்றுமதி

கச்சா வெள்ளாட்டுத் தோல் ஏற்றுமதிக்காக சென்ற ஆண்டு வகுக்கப்பட்ட முறையை 1962 (ஜனவரி-டிசம்பர்) ஆண்டுக்கும் தொடர்ந்து அமல் நடத்துவது என்று இந்திய சர்க்கார் முடிவு செய்துள்ளது.

இம்முறையின் அம்சங்களாவன :

1. பல ஆண்டுகளாக ஏற்றுமதி செய்து வருபவர்களுக்கு, 1954 முதல் 58 முடியவான 5 ஆண்டுகளுக்குள் எந்த ஆண்டில் அவர்கள் ஏற்றுமதி அதிகமாக இருந்ததோ அதில் 6½% கோட்டா வழங்கப்படும்.
2. 1959-ம் ஆண்டு ஏற்றுமதி செய்து, 1961ல் ஏற்றுமதி செய்யாதவர்களின் ஏற்றுமதிக்கான விண்ணப்பம் தகுதி அடிப்படையில் ஆலோசனைக்கு எடுத்துக் கொள்ளப்படும்.
3. ஏற்றுமதியாளர்களில் 1,50,000 தோல்களுக்கும் குறைவாக ஏற்றுமதி செய்வோருக்கு, அவர்கள் அடிப்படை ஏற்றுமதியில் 100% ஏற்றுமதி செய்ய அனுமதி அளிக்கப்படும். 1,50,000 தோல்களுக்கு மேல் ஏற்றுமதி செய்பவர்களில் எவருடைய ஏற்றுமதி இப்புதிய ஏற்பட்டால் குறைகிறதோ அவர்களும் 1,50,000 தோல்கள் ஏற்றுமதி செய்ய அனுமதிக்கப்படுவர்.
4. 1,50,000 தோல்கள் அல்லது அதற்குக் குறைவாக ஏற்றுமதிக்குக் கோட்டா அளிக்கப்படுவர்கள், விரும்பினால் கோட்டா உள்ள மற்றவர்களோடு கூட்டுச் சேர்ந்து தங்கள் கோட்டாக் களை லாபகரமாகப் படன் படுத்திக் கொள்ளலாம்.

ஆதாரம்-''எகனமிக்ஸ் டைம்ஸ்'' ஜன. 1962.

**ஒட்டுண்ணிகள், அவற்றால் உண்டாகும்
நோய்கள்பற்றிய ஆலோசனைக் கூட்டம்**

(Conference on parasites and parasitic diseases)

இந்திய வரலாற்றிலேயே முதன் முதலாக, கால்நடை ஒட்டுண்ணி ஆராய்ச்சியாளர்கள் சென்ற ஆண்டு செப்டம்பர் 19-ம் தேதி முதல் 22-ம் தேதி வரை சென்னையில் ஆலோசனைக்காகக் கூடினர். மனித ஒட்டுண்ணி ஆராய்ச்சியாளர்களில் சிலரும் இக்கூட்டத்தில் கலந்து கொண்டனர். இக்கூட்டம் இந்திய விவசாய ஆராய்ச்சிக் கழகத்தின் (Indian Council of Agricultural Research) ஆதரவில் நடைபெற்றது. கூட்டத்தை சென்னை சர்க்காரின் விவசாய, கால்நடை மந்திரி கனம் எம். பக்தவத்சலம் அவர்கள் துவக்கி வைத்தார்கள். இந்திய சர்க்காரின் சார்பில் கால்நடை வளர்ச்சிக் கமிஷனர் ஸ்ரீ. எல். ஷஹாய் அவர்கள் கலந்து கொண்டு கூட்டத்திற்குத் தலைமை தாங்கினார்கள்.

கூட்டத்தைத் துவக்கிவைத்து ஸ்ரீ பக்தவத்சலம் அவர்கள் பேசியபோது இந்தியாவைப் போன்ற வெப்ப நாடுகளில் கால்நடைகளை நோயற்றதாக வைத்திருப்பதே பெரிய பிரச்சனையாக உள்ளது. ஒட்டுண்ணிகளால் ஏற்படும் நோய்களால் பாதிக்கப்படும் கால்நடைகள் மூலம் அவற்றை வளர்ப்பவர்கள் பெருத்த நஷ்டமடைகிறார்கள் என்று கூறினர். அவர் மேலும் பேசுகையில் கால்நடைகளுடன் நெருங்கிய தொடர்பு கொண்டு அவற்றை உணவுக்காகப் பயன்படுத்துபவரும் இந்த ஒட்டுண்ணிகளால் பாதிக்கப்படுகிறார்கள் என்றும் தெரிவித்தார்.

தமது தலைமை உரையில் ஸ்ரீ ஷஹாய் அவர்கள் சென்ற சில தலைமுறைகளாகவே பாக்கிரியாக்களால் ஏற்படும் நோய்கள்பற்றிய ஆராய்ச்சியில் சிறந்த கவனம் செலுத்தப்பட்டு வந்துள்ளது. இதன் மூலம் நோய்களைக் கட்டுப்படுத்துவதில் இன்று சிறந்த வெற்றி ஏற்பட்டுள்ளது. ஒட்டுண்ணிகள் பற்றிய ஆராய்ச்சி நடைபெற்றுவந்த போதிலும், இதன் மூலம் ஏற்படும் நோய்தடுப்புத் துறையில் இன்னும் முழு கட்டுப்பாடு காண வழி கோலப்படவில்லை. இந்நிலையை அடைய பெருத்த முயற்சியும் அதிகமான பணவசதியும் தேவைப்படுகிறது என்றும் எடுத்துரைத்தார்.

ஆதாரம்: 'இந்தியன் வெடர்னரி ஜெர்னல்', பிப்ரவரி, 1962.

**உலக வெள்ளாட்டுத் தோல் வியாபார நிலை
அமெரிக்காவுக்கான ஆட்டுத்தோல் இறக்குமதி**

அமெரிக்காவிலுள்ள பதனிடு நிலையங்களில் வெள்ளாட்டுத் தோல்களுக்கான தேவை தொடர்ந்து குறைந்ததால் 1961-ம் ஆண்டு ஏப்ரல்-மே. மாதங்களுக்கான இறக்குமதி முந்தைய ஆண்டில் இதே மாதங்களை விட 35 சதவீதம் குறைந்தது. 1961-ம் ஆண்டு ஆரம்ப முதல் இறக்குமதி 1960-ம் ஆண்டு இதே மாதங்களில் இருந்ததை விட \$ பாகம் குறைந்தது. ஜனவரி-மார்ச் மாதங்களில் காமன்வெல்த் நாடுகளிலிருந்து இறக்குமதி அதிகரித்தும், ஏப்ரல்-மே மாதங்களில் குறைந்ததால் மொத்த இறக்குமதி அதிகம் மாறவில்லை. இருப்பினும் ஜனவரி-மே மாதங்களுக்கான இறக்குமதி மொத்தத்தில் 68 சதவீதமாக இருந்தது. 1960-ம் ஆண்டில் இது 47 சதவீதமாக இருந்தது.

1958, 59-ம் ஆண்டுகளில் அமெரிக்காவுக்கு அதிக அளவில் தோல்களை ஏற்றுமதி செய்த நாடுகளில் இரண்டாவது இடம் வகித்த பிரேசில் நாட்டிலிருந்து அமெரிக்காவுக்கான இறக்குமதி தொடர்ந்து குறைந்து வந்தது. எதியோப்பியா, ஈரான் ஆகிய நாடுகளிலிருந்து இறக்குமதி செய்த அளவும் குறைந்தது. (அட்டவணை - 1)

ஆதாரம்: 'டேனர், நவம்பர், டிசம்பர், 1961.

**கிழக்கிந்திய முறைப்படி பதனிடப்பட்ட
ஆட்டுத்தோல் ஏற்றுமதி குறிப்பிட்ட அளவைவிட
அதிகமாயிற்று**

1960-61ம் ஆண்டில் ஏற்றுமதி செய்யப்பட்ட ஆட்டுத் தோல்களின் எண்ணிக்கை அவ்வாண்டு குறிப்பிடப்பட்டிருந்த அளவைவிட அதிகமாயிற்று என்று தோல் ஏற்றுமதி அபிவிருத்திக் கழகம் (Leather Export Promotion Council) அறிவித்துள்ளது.

கிழக்கிந்திய முறைப்படி பதனிடப்பட்ட வெள்ளாட்டுத் தோல்களின் ஏற்றுமதி மதிப்பு குறிப்பிட்ட அளவைவிட ரூ. 14,200,000 அதிகமாயிற்று. செம்மறியாட்டுத் தோல்களின் ஏற்றுமதி மதிப்பு ரூ. 8,800,000 அதிகமாயிற்று. தோல் ஏற்றுமதியின் மொத்த மதிப்பு குறிப்பிட்ட அளவைவிட ரூ. 16,600,000 அதிகமானாலும் பசுத்தோல், ஒப்பனை செய்யப்பட்ட தோல் (finished leathers) ஆகியவைகளின் ஏற்றுமதி மதிப்பு குறிப்பிட்ட அளவைவிட மிகவும் குறைந்தது. 1960-61ம் ஆண்டு ஏற்றுமதிக்காகக் குறிப்பிட்ட அளவு, ஏற்றுமதியான அளவு, குறைவு, நிறைவு பற்றிய விவரங்களை அட்டவணை 2ல் காணலாம்.

ஆதாரம் 'டேனர்', பிப்ரவரி, 1962.

அட்டவணை-1
அமெரிக்காவுக்கான ஆட்டுத்தோல் இறக்குமதி

நாடுகள்	1959		1960		1961		
	ஜனவரி- டிசம்பர்	ஜனவரி- மார்ச்	ஏப்ரல்- ஜூன்	ஜூலை- டிசம்பர்	மொத்தம்	ஜனவரி- மார்ச்	ஏப்ரல்- ஜூன்
இந்தியா	4,206	496	785	1,725	3,006	725	569
பிரிட்டிஷ் கிழக்கு } ஆப்பிரிக்கா }	1,012	191	404	167	762	3	23
நைஜீரியா	1,475	169	513	935	1,617	314	259
பாகிஸ்தான்	1,920	564	649	1,318	2,531	643	388
இதர காமன்வெல்த் } நாடுகள் }	198	218	85	81	384	25	15
அர்ஜென்டினா	641	111	162	100	373	32	6
பிரேசில்	1,973	455	386	273	1,114	257	209
சிலி	110	31	47	29	107	15	12
காங்கோ குடியரசு	123	18	12	26	56	—	—
எதியோப்பியா	1,674	271	223	55	549	98	73
இந்தோனேஷியா	155	31	58	64	153	24	10
சுரான்	675	95	388	242	725	174	99
சுராக்	86	38	—	—	—	—	—
பெரு	756	195	207	396	798	136	56
சோமாலியா	558	116	148	—	264	—	31
சூடான்	51	11	18	14	43	7	5
இதர நாடுகள்	872	221	244	255	720	60	99
மொத்தம்	16,485	3,231	4,329	5,680	13,240	2,513	1,854

அட்டவணை-2

கிழக்கிந்திய முறைப்படி பதனிட்ட தோல்களின் ஏற்றுமதி

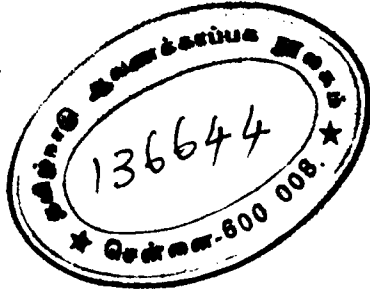
தோல்களின் வகைகள்	ஏற்றுமதி குறிப்பிட்ட அளவு (லட்சத்தில்)	ஏற்றுமதி யானது (லட்சத்தில்)	குறைவு/அதிகம் (லட்சத்தில்)
1. பதனிட்ட எருமைத் தோல்கள்	24.40	22.25	2.15
2. பதனிட்ட பசுத் தோல்கள்	601.40	511.63	89.77
3. பதனிட்ட எருமைக் கன்றுத் தோல்கள்	107.00	101.74	5.26
4. பதனிட்ட பசுங்கன்றுத் தோல்கள்	107.20	86.16	21.04
5. பதனிட்ட 'கிப்ஸ்' (Kips)	13.00	17.98	4.98
6. பதனிட்ட வெள்ளாட்டுத் தோல்கள்	669.70	811.59	141.89
7. பதனிட்ட செம்மறியாட்டுத் தோல்கள்	651.30	739.07	87.77
8. பாம்பு-உடும்பு போன்ற ஊர்வனவற்றின் தோல்கள்	12.00	9.38	2.62
9. ஒப்பனை செய்யப்பட்ட தோல்கள்	214.00	184.78	29.22
10. தோல் காலணிகள் (பூட்ஸ்-ஷூக்கள்)	270.00	263.94	6.06
11. இதர தோல் சாமான்கள்	18.50	15.08	3.42
12. வெள்ளாட்டு உரோமம்	100.00	41.51	58.49
மொத்தம்	2,788.50	2,805.11	16.61

நிலையச் செய்திகள்

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