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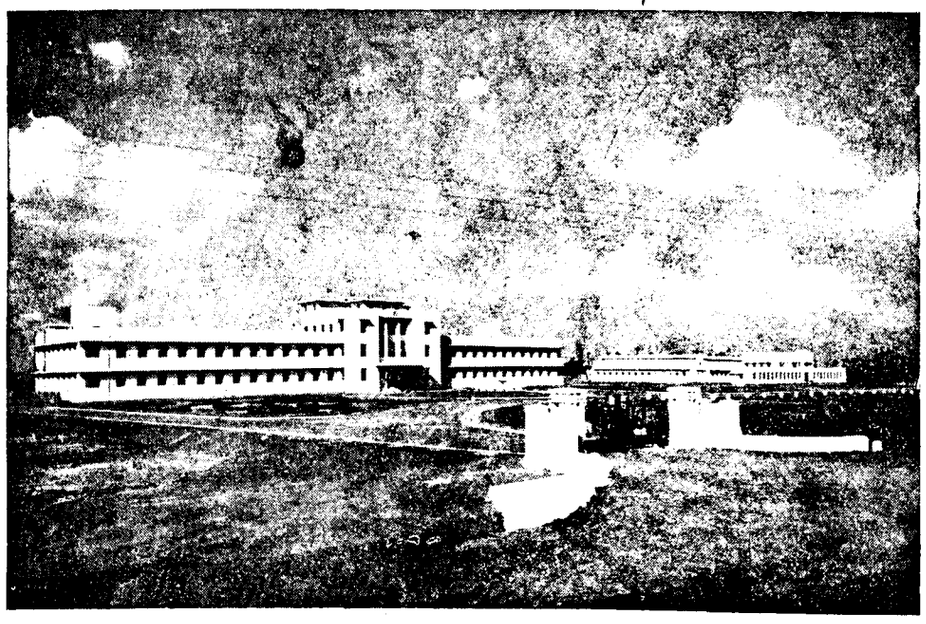

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

INDIA

THE EFFECT OF ACIDS AND SALTS IN VEGETABLE TANNING—Part I:

The Effect of some Salts in Sole Leather Tannage:

Y. NAYUDAMMA, K. S. JAYARAMAN & T. S. KRISHNAN.

SUMMARY

The effect of acids and salts when they are used for the pre-treatment of the pelt or added to the tan liquor in vegetable tanning is discussed. The assessment has been made on the physical properties such as colour, crackiness, solidity, tightness, etc., of the finished leathers, hydrothermal stability and penetration of tannin during the course of tanning. Chemical assessment has also been made stratigraphically with regard to water solubles, oils and fats, fixed tannin, leather content and degree of tannage and compared with the control which has not been subjected to any pre-treatment.

Numerous researches have been made[1-8] to study the influence of acids and salts in vegetable tannage. The different anions may vary in their valency, their lyotropic effects or their tendency to fix on collagen. Anions which have a strong tendency to fix on fibres increase their acid up-take at a given pH—,diminishing their swelling and permit hydrolytic changes. The fibre structure, plumping, the net charge on the protein and the tannin fixation are shown to be interrelated. Such factors are in turn related to effects of acids and salts. Acids and salts affect the characteristics of both collagen fibre and the tanning compound, thus controlling the rate of penetration, fixation of tannin and yield and colour of the leather. Thus the importance of pH and concentration of acids and salts in vegetable tanning, has been fully recognized.

The extensive work conducted in this field has only indicated, that still much remains to be done. Rapid tanning methods of sole leather involve the successful use of mechanical aids or suitable modification of the protein or the tannin, for rapid penetration and fixation of tannin. As stated earlier, acids and salts exercise such an influence. In tanning practice, acids and salts may be used for the pre-treatment of the pelt before tanning or may be added to the tan liquor, prior to tanning or during the course of tanning. A preliminary study by one of us[9] has shown that the pre-treatment of pelt with sod. acetate, citrate, calgon and dichromate adjusted to a pH 4.8 prior to tanning will

The tanned pieces from each set were taken out. Out of the two pieces in each experiment one piece was further treated with 30 Bk. myrobalan liquor for a period of 3 days.

FINISHING :

The tanned pieces from each set were taken out, scoured, washed, beamed, set, lightly oiled on the surface and air-dried.

The dried pieces were weighed and taken for physical, chemical and stratigraphic assessment.

ANALYTICAL :

During the course of tanning : In each set, during tanning, the rate of penetration, color and shrinkage temperature were noted.

Physical assessment : The dried leathers were tested for their physical properties like general appearance, colour, grain crackiness, tightness, solidity, uniform penetration of tannin, weave pattern and cheesy cut.

Physical properties : The dried leathers were tested for shrinkage temperature, tensile strength and the yield.

Chemical properties : A portion of leathers were ground and analysed for moisture, hide substance, oils and fats, total ash, insoluble ash, water solubles, pH of water solubles, degree of tannage and leather substance by standard methods.

Stratigraphic analysis : A portion of the wattle tanned (unmyrobed) leathers were split into 3 layers (grain, middle and flesh) ; the weights of each of which were noted and chemically analysed. The results are presented in a stratigraph form.

The data relative to the stratigraphic unmyrobed wattle samples are discussed in Part I of these studies.

DATA AND DISCUSSION :

RELATIVE TO WATTLE TANNAGE :

OBSERVATION DURING THE COURSE OF TANNING :

Rate of penetration of tannin : The rates of penetration on visual observation are recorded in Table I below :

TABLE I—Rate of Penetration

15°Bk NaX + NaCl + H_2SO_4	Series	I	Oxalate Citrate	> Acetate Formate	Lactate > Tartrate Calgon	> $NaCl + H_2SO_4$ Control	> Dichromate	
NaX + HX	,,	II	Calgon Formate	> Oxalate Citrate Lactate	> Tartrate Acetate	> $NaCl + H_2SO_4$ Control	> Dichromate	
NaX added to the liquor	Series	III	Citrate	> Oxalate Lactate	> Acetate Formate	> Calgon Tartrate Control	> Dichromate	
30°BK	Series	I	Oxalate Citrate Acetate	> Formate Calgon	> Lactate Tartrate	> $NaCl + H_2SO_4$ Control Dichromate		
	,,	II	Calgon Citrate Formate	> Acetate Oxalate Lactate	> Tartrate	> $NaCl + H_2SO_4$ Control Dichromate		
	,,	III	Citrate Oxalate Acetate	> Lactate Formate Calgon	> Tartrate	> Control Dichromate		
45°BK	,,	I	Oxalate Citrate Acetate (Full) Formate Calgon	> Lactate Tartrate $NaCl + H_2SO_4$ Dichromate Control	(Slight streak)			
	,,	II	Calgon Citrate Formate (Full) Acetate Oxalate	> Lactate Tartrate $NaCl + H_2SO_4$ Dichromate Control	> (Slight streak)			
	,,	III	Citrate Oxalate Acetate (Full) Formate Calgon	> Lactate Tartrate	Control > (Slight)	Dichromate > (Slight)		
09°BK			All penetrated					

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reduce the period of tanning. Based on this information, processes have been worked out for the rapid tannage of sole leather[10] and E.I. tanning of kips and skins[11, 12]. The rapid tanning methods for sole leather tannage are gaining ground in the tanning trade and a systematic study at this time on the effects of acids and salts on the course of tanning and the properties of tanned leather should be of interest. It is with this view, work has been undertaken to study the effect of a number of sodium salts of organic and inorganic acids, namely, sodium formate, acetate, lactate, citrate, tartrate, oxalate, dichromate and calgon. These salts were used for treatment of the pelt as well as for treatment of the tanliquors before tanning. The chemical, physical and stratigraphic analyses of the leathers were determined and the results are reported as Parts I—III of these papers. In Part I of these studies, the stratigraphic analytical data relative to the effects of salts on straight wattle tannage are discussed.

Experimental :

The butt portion of wet salted buffalo hide was soaked for 3—4 hrs., washed thoroughly in different changes of water. The well-soaked and washed material was limed with 15% lime and 1% Na_2S (on the soaked wt.) and sufficient amount of water and handled for 3 days. On the 4th day, the goods were unhaired, put into a fresh bath containing 10% lime (on soaked wt.) and sufficient water; kept for 3 days, handling each day. On the 7th day, the well plumped material was fleshed, scudded well and washed. The pelt was then split to uniform thickness and cut to uniform size and later completely delimed with boric acid. The delimed pelt was washed repeatedly with water and drained. The delimed weight was noted.

(*a*) Control : A portion of fully delimed pieces (4 Nos.) were taken directly to tanning with wattle liquor.

(*b*) *Pretreatment of the pelt* : ($NaCl + H_2SO_4$ system).

A portion of fully delimed pieces (2 Nos.) were pre-treated with 10% NaCl and sufficient acid (H_2SO_4) to arrive at an equilibrium pH 4.8. The equilibrium was attained in 36 hrs. and at the end of this period, the pre-treated pelt was taken out for tanning.

Pretreatment of the pelt : (*$NaCl + H_2SO_4 + NaX$ system*) :

Series I : A portion of the fully delimed pieces were pre-treated with 10% NaCl + 5% NaX (where X stands for formate,

acetate, oxalate, citrate, lactate, tartrate, dichromate and calgon) and sufficient amount of H_2SO_4 to adjust the pH to the equilibrium pH 4.8. For each system, 2 cut pieces were taken. The pieces were thus pickled for 36 hrs. adjusting the pH of the system with H_2SO_4 repeatedly to arrive at an equilibrium pH 4.8. At the end of this period, the pickled pieces were taken out for tanning.

Pretreatment of the Pelt :

(*$NaX + HX$ system*) : *Series II* : In this series, the delimed pieces were treated with 5% NaX (the same salts as in Series I) and the requisite amount of acids corresponding to the anion of the salt X (namely formic acid, acetic acid etc.,—in case of calgon and dichromate, only H_2SO_4 was used). This series is different from Series I in that it is a buffer system where salts of organic acids were used (salt of a weak acid + weak acid except in case of calgon and dichromate). The goods were pickled to an equilibrium pH 4.8 over a period of 36 hrs. At the end of this period, they were taken out for tanning.

Pretreatment of Tanliquor :

Series III : The delimed pieces were not pre-treated in this case as in the two previous series. Instead, the same salts used in the above series were added to the tanliquor. The tanning was conducted with wattle liquors of 15°, 30°, 45°, 60°, 75°, 90°Bk liquors, starting with 15°Bk and increasing the Bk strength by 15°, every alternate day. To each one of these liquors the salts were added—0.5% on the delimed pelt weight or 0.1% w/v on the tanliquor).

Tanning :

In all cases, wattle liquor was used and the liquor to material ratio was kept at 5:1. The tanning was conducted by suspending the goods in a battery jar for each experiment.

The tanning was started with a tanliquor of 15°Bk strength. Every alternate day, the strength of the liquor was increased by 15°Bk. The final liquor was 90°Bk in which the goods were kept for 2 days. The pH of tanning was controlled starting at pH 4.5 and reducing it by 0.2 units every alternate day along with the increase in Bk strength, completing the tannage with a final pH 3.5. The pH was adjusted in all the systems with sulphuric acid except in case of Series II, where the pH was adjusted by the acid corresponding to the anion of the salt used for pre-treatment of the pelt.

It had been realised for many years that salts assist the penetration of tannin. From a study of the table, it is observed that certain salts help the rate of penetration while others do not. The penetration was complete in 6 days in case of calgon, citrate, formate and acetate, whether the salts were used for pretreatment of the pelt or added to the liquor. However, in case of lactate, tartrate, dichromate and NaCl systems, the rate of penetration was slow, particularly so in case of dichromate treatment. The penetration was complete in all these cases along with the control in eight days. Evidently, salts of hydroxy acids (excepting citrate) do not help the rate of penetration of tannin when they are used either for the pretreatment of the pelt or the liquor, whereas salts of mono-, di-, or tricarboxylic acids do help the speed of penetration. Similarly, certain inorganic salts impede the rate of penetration while others like calgon increase it.

The salts that help the rate of penetration are citrate, calgon, formate, acetate and oxalate. Even amongst these salts, the rate of penetration varies depending upon the mode of their addition to the pelt or the tanliquor. This may be seen from Table I. When calgon is used for pre-treatment of the pelt, by itself, the rate of penetration is rapid even on the first day (Series II) but if salt is present, the rate of penetration catches up with others only the 6th day ; similarly when it is added to tanliquors. But it is to be noted that the total period taken for complete penetration of tannin is the same whether the salt is added to the pelt or tanliquor. Evidently, apart from the mode of addition, the concentration of the salt present in the system will also govern the rate of penetration. A study on the effect of concentration of the salt for the penetration of tannin into the pelt should be of interest.

To improve the rate of penetration, amongst these salts citrate is most effective when added to tanliquors ; calgon and formate when used for pre-treatment of the pelt and oxalate and citrate when used along with NaCl for pre-treatment of the pelt under the set of conditions is under study.

Shrinkage temperature during the course of tanning.

The shrinkage temperature of the fully delimed pelt was 60°C. Shrinkage temperature was noted every alternate day during the course of tanning when the strengths of tanliquor was increased and the pH of tanning decreased. The data so collected are given in Table II.

TABLE II

SHRINKAGE TEMPERATURE

Ts °C

	°Bk strength of liquor						
	15	30	45	60	75	90	Dry.
$NaCl + H_2SO_4$	88	89	90	89	82	82	81
Series I : $(NaCl + H_2SO_4 + NaX)$							
Sod. Acetate	83	89	86	85	82	82	81
,, Formate	84	87.5	86	84	82	82	82
,, Oxalate	75	87	87	83	82	81	82
,, Citrate	84	87	87	85	82	82	82
,, Lactate	78	88	88.5	86	83.5	82	82
,, Tartrate	80	89	88	86	83	82	81
Calgon	81	88.5	90	86	84	82	82
Sod. Dichromate	80	92	91	89.5	89	85	84
Series II : $(NaX + HX)$:							
Sod. Acetate+acetic acid	86	90	88	88	82	82	82
,, Formate+formic ,,	86	88	85	88	82	82	83
,, Oxalic+Oxalic ,,	89	88	84	87	81	82	82
,, Citrate+Citric ,,	88	88	85	87.5	82	82	81
,, Lactate+Lactic ,,	89	88.5	85	88	82	83	82
,, Tartrate + Tartaric ,,	88.5	88	85	87	83	84	81
Calgon+H_2SO_4	87	90	85	88	83	83.5	81
Sod. Dichromate+H_2SO_4	89	94	91	90.5	84	85	83
Series III : *Pre-treatment of tanliquor* : (Addn. of salts) :							
Control (No salt)	84.5	86	89	91	81.5	80	80
0.5% Sod. acetate	74	88	88	86	81	81	81
,, Formate	75	88.5	89	88	83	80.5	81.5
,, Oxalate	88	88	89	88.5	81	80	81
,, Citrate	86	88	89	89	83	81	81
,, Lactate	85	88	89	89	82	81	81
,, Tartrate	77	88.5	90	90	83	81	80
Calgon	79.5	88.5	90	90	83	82	83
0.5% Sod. Dichromate	73	88.5	82	91.5	85	85	82

From a consideration of this table, the following observations are made.

The shrinkage temperature increased from 60°C. to 73-88°C. in the first two days. Thereafter, there is an increase up to 8th day or 6th day till the tannin is completely penetrated throughout the hide ; but that increase is only

very slight. Attaining a maximum shrinkage value, the shrinkage temperature is once again decreased markedly and then remains constant, with the increase in the period of tanning and strength of the tanliquor. This trend is the same in all cases (control as well as salt systems).

This interesting observation confirms some of the findings of earlier workers. The shrinkage temperature is increased with the increase in the fixed tannin and degree of tannage up to a certain extent. With further increase in the degree of tannage, the shrinkage temperature remained constant when the degree of tannage was 30 and above,[13] or even leads to a slight lowering of the shrinkage temperature. This lowering is attributed to a breaking up of hydrogen bonds of the paptide groups by vegetable tannins fixed without cross-link formation.[14] This fact is clearly demonstrated by these data.

Control : The initial value at the end of 2 days tanning was 84.5°C and the maximum value obtained for the control was 91°C. on the 9th day (just after the tannin had completely penetrated and on further tanning the shrinkage temperature decreased). At the completion of tannage, the wet leather and dried leather had a lower shrinkage temperature at 80°C.

$NaCl + H_2SO_4$ system : The shrinkage temperature of the final wet and dry leathers were 82° and 81°C.—slightly higher to that of control. The shrinkage temperature values were actually high throughout the course of tanning as compared to control. The initial value was quite high at 88° and the highest value 90° was reached after 6 days.

$NaCl + H_2SO_4 + NaX$ systm : The initial values varied from 75° (lowest in case of oxalate) and 84° (in case of formate and citrate) and the highest values were reached at the end of 6 days in all cases. The highest shrinkage temperature values were recorded for dichromate 91°C and calgon 90°C and the others varying from 86-88°. These values were gradually reduced on further tanning to 82°.

Evidently the salts of inorganic acids like NaCl, calgon and dichromate increase shrinkage temperature as compared to salts of organic acids ; but the final shrinkage temperature values for dry leathers are approximately the same for all salts except in case of dichromate where there is a slight increase due probably to basic chrome salt formed.

NaX + HX SYSTEM : SERIES II :

The initial values after 2 days tanning are the highest in these series, as compared to other series and control. The initial shrinkage temperature varied from 84° lowest in case of oxalate and 89° in case of dichromate. The effect is very similar to that observed in Series I. The shrinkage temperature values increase up to 4-6 days reaching a maximum at 88-94° and again decreasing to 82-85°. The shrinkage temperature values for dry leathers vary from 81-83°.

NaX ADDED TO TANLIQUORS : SERIES III :

The initial values after the first 2 days tanning were the lowest compared to other series varying from 73-88°. However, after 4 days, the values are approximately the same for all salts. The maximum values were reached after 6-8 days followed by a decrease on further tanning. The final values for wet and dry leathers were between 80-82°C similar to control and lowest as compared to other series.

PHYSICAL ASSESSMENT :

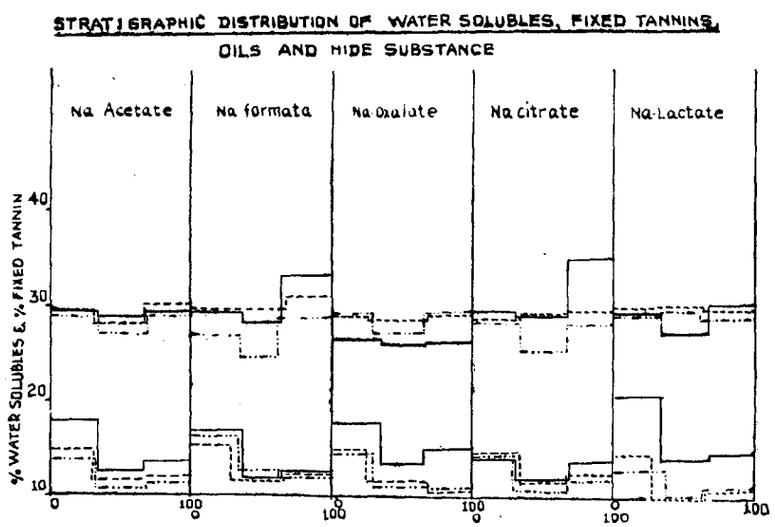
The control experiments (no salts) gave a leather that is solid, fairly tight with uniform penetration of tannin, cheesy cut and good grain characteristics. But the colour was not good and the general appearance fair. As compared to this control, the leathers obtained where salts were used in all the series, were equal to if not better in all these respects. The colour and general appearance of leathers from the salt series were in fact much better to that of control. The leathers from Series II (NaX + HX) system were actually adjudged to be the best of the lot indicating the specific effect of single anions.

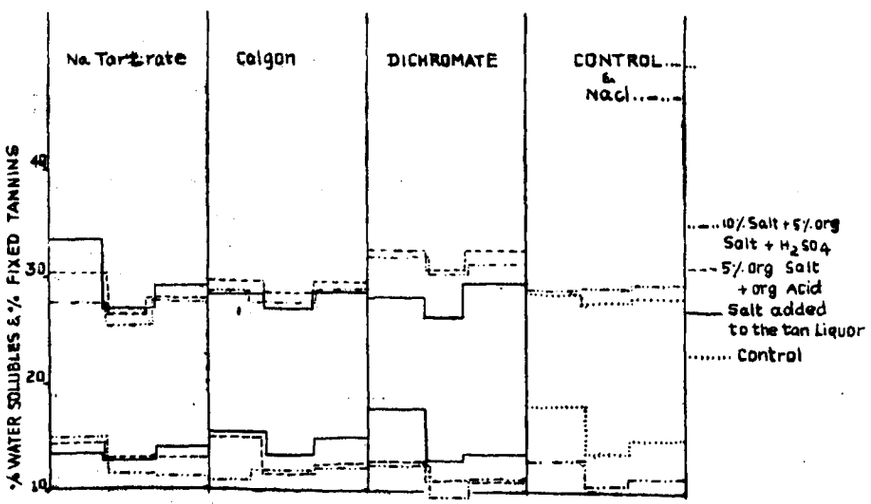
The colour of the leather which is an important factor in sole leather tannage is much improved in case where sod. acetate and calgon were used for pre-treatment of the pelt in Series I & II, as compared to other salts. When salts were added to tanliquors, the colour is not improved to the same extent as in case where salts were used for pre-treatment of the pelt.

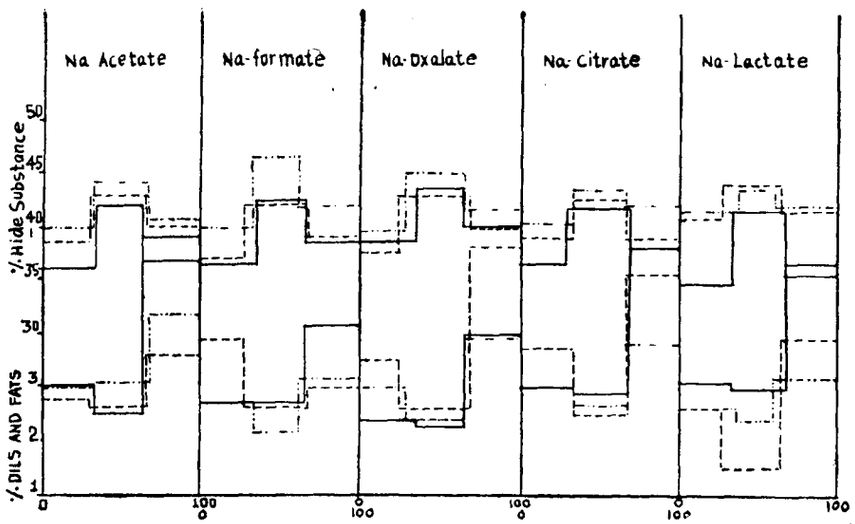
STRATIGRAPHIC ANALYSIS :

The wattle tanned leathers were split into 3 layers—grain, middle and flesh layers—the weights of which were noted and the results expressed in the stratigraph on the basis of layer weights.

Fig. 1


STRATIGRAPHIC DISTRIBUTION OF WATER SOLUBLES, FIXED TANNINS, OILS AND HIDE SUBSTANCE
Na Acetate
Na formata
Na Oxalate
Na citrate
Na-Lactate
% WATER SOLUBLES & % FIXED TANNIN
40
30
20
10
0
100


Na Tartrate
Calgon
DICHROMATE
CONTROL & Nacl
% WATER SOLUBLES & % FIXED TANNINS
40
30
20
10
10% Salt + 5% org Salt + H_2SO_4
5% org Salt + org Acid
Salt added to the tan Liquor
Control


Na Acetate
Na-formate
Na-Oxalate
Na-Citrate
Na-Lactate
% Hide Substance
% OILS AND FATS
50
45
40
35
30
3
2
1
0
100

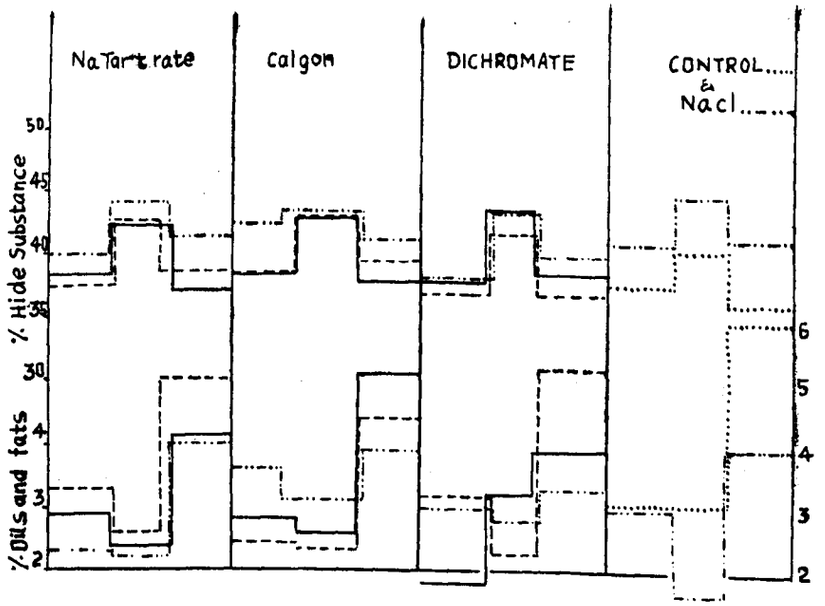
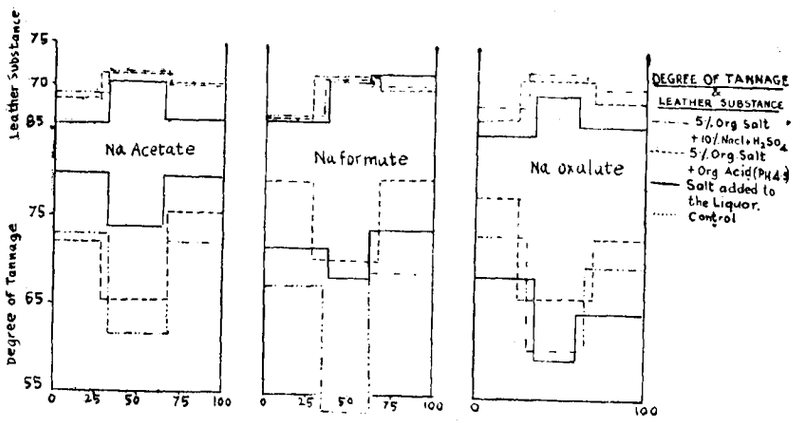
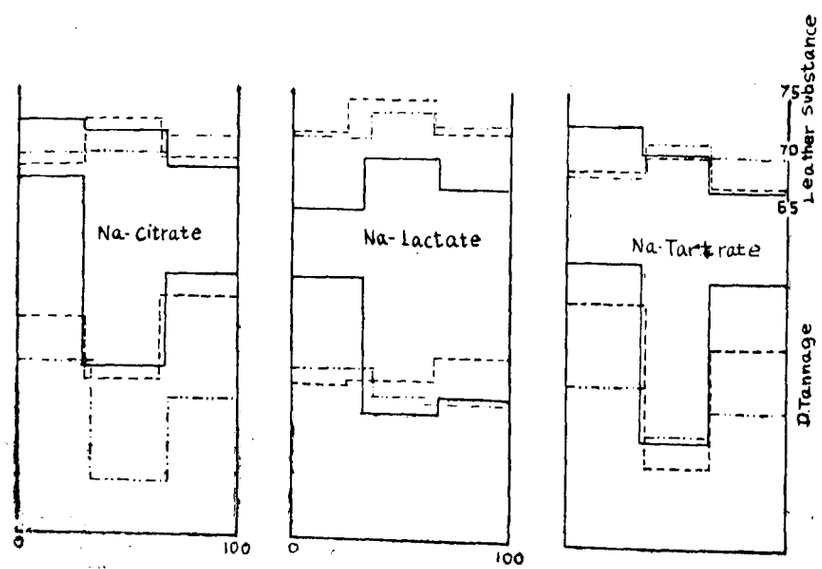
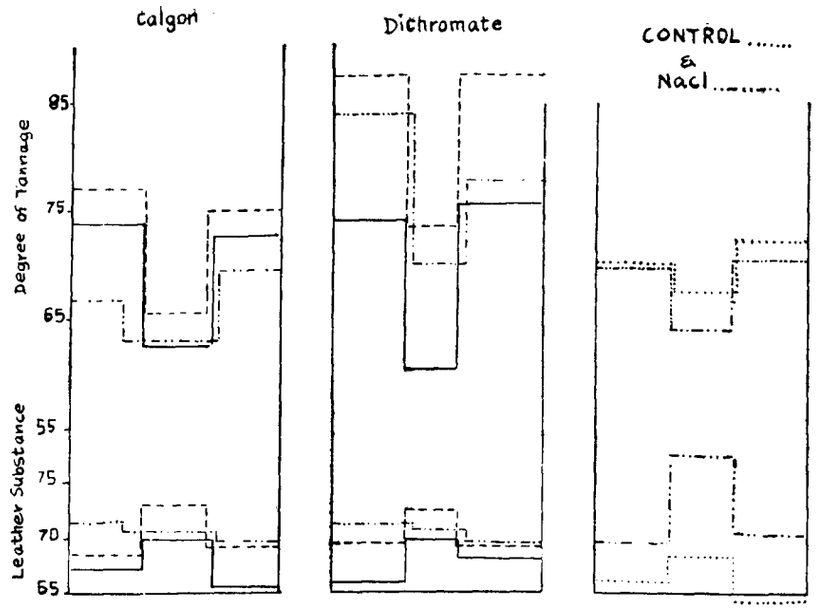

Na Tartrate
Calgon
DICHROMATE
CONTROL & Nacl
% Hide Substance
% Oils and fats
50
40
30
4
3
2
6
5
4
3
2

Fig. 2







From the stratigraph given below, the following observations are made :

WATER SOLUBLES :

(1) In all cases, the water solubles content is high on the grain, low in the middle and flesh layers. The water solubles content in flesh is slightly higher or equal to that of the middle layer.

(2) In the control experiment, the water solubles content is highest in the grain at 18%, 13.6% middle and 14% on the flesh layers.

(3) As compared to control, the values obtained for NaCl—H_2SO_4 system are lower in all the layers.

(4) As compared to the control, the values obtained in Series I are consistently lower in all cases. The values are very close to those obtained in NaCl system as above. The values obtained for this series are the lowest in comparison with other series. The water solubles content is uniform in all the layers in case of calgon.

(5) In Series II where NaX is added, the values tend to be slightly higher to that of NaCl systems but still considerably lower to that of the control. The values tend to be uniform in all layers in case of tartrate and dichromate. In case of calgon

and dichromate, the water solubles content is lower in Series I as compared to Series II, indicating the specific effect of NaCl to reduce water solubles content.

(6) In Series III, the water solubles content is slightly lower to that of the control except in case of lactate, oxalate and acetate, particularly on the grain layer ; but the values are much higher than those obtained in other series. The water solubles content is low as well as uniform in case of tartrate, calgon and citrate in this series.

It is clear that addition of salts to tanliquors will not help to reduce water soluble contents of leathers to any great extent. But when they are used for pre-treatment of the pelt, there is a reduction of water solubles content and this effect is more pronounced where NaCl is present.

FIXED TANS :

(1) The fixed tannin content is uniform throughout the layers in case of control. The value is 28%.

(2) The fixed tannin content is slightly higher in case of NaCl plus H_2SO_4 system and is also uniform throughout the layers as in control.

(3) In case of $NaCl + H_2SO_4 + NaX$ system, the general trend is that the grain and flesh layers contain the same amount of fixed tannin and the middle layer contains a lesser amount. Such is the case with regard to all salts except lactate and to an extent calgon where the fixed tannin contents are uniform throughout the 3 layers.

Amongst these salts, the highest values for fixed tannin were obtained in case of dichromate and lowest in case of formate.

(4) In NaX + HX system, the values for fixed tannin tend to be higher as compared to the control as well as in Series I in all cases. The highest values are again obtained in case of dichromate. The general tendency is that fixed tannin is fairly uniform throughout the layers except in case of tartrate.

(5) *Series III—NaX added to tan liquors* : The values tend to be higher than the control in most cases except with dichromate, lactate and oxalate. The fixed tannin content is not uniform in all layers. The general trend is to fix more tannin on the flesh layer (contrary to Series I) except in case of tartrate, where more tannin is fixed on the grain side.

(6) Formate behaves somewhat different from other salts in that whatever be the mode of its addition for pre-treatment of the pelt or tanliquors, the tannin fixation is greater on the flesh side as compared to other layers.

(7) For uniform penetration and fixation of tannin NaX—HX treatment of the pelt appears to give best results with all salts.

OILS AND FATS :

In sole leather tannage, oil is applied only on the surface. The oil content, therefore, will be more on the surface layers as compared to the middle layers. This is clearly brought out in the stratigraph.

(1) In case of control the oil content on the grain and middle layers is equal but very much less than that obtained in flesh layers. On the flesh layer, the oil content (6%) is approximately double that of grain and middle layers.

(2) In $NaCl + H_2SO_4$ system, the tendency is for the flesh layer to contain more than the grain layer which, in turn, is more than the middle layer.

(3) In $NaCl + H_2SO_4 + NaX$ system (Series I), the trend is the same as in NaCl system except that the oil content is more uniform in all the layers. As compared to any other series, the oil distribution is more uniform in this series. This effect is more pronounced in case of calgon and dichromate.

(4) NaX + HX system (Series II)—similar to $NaCl + H_2SO_4$ system but the fixation of oil is much greater in all the layers and more so on flesh layer. The fixation is not uniform as in Series I.

(5) NaX added to tanliquors (Series III)—The general trend is similar to control where the flesh layer fixes a great amount of oil as compared to grain and middle layers containing the same amount of oil, except in case of dichromate.

The results do not warrant any general conclusions because oiling is a physical process. It appears, however, that where pelt is pre-treated with salts, there is a tendency for the oil to penetrate more into the leather and oil distribution is more uniform throughout the thickness of leather.

The values for degree of tannage and leather contents are presented in Fig. 2.

DEGREE OF TANNAGE : (D.T.)

(1) In the case of control, D.T. is slightly higher on the flesh layer to that of grain which is in turn higher to that of middle layer. The range is 67-72%.

(2) In NaCl + H_2SO_4 system, the grain and flesh layers have a uniform D.T. but the middle layer has a much less figure for D.T.64 as compared to 70 in other layers. These values are also slightly lower to that of control.

(3) In NaCl + H_2SO_4 + NaX system :—Series I : The D.T. values are lower to that of control in many cases except dichromate. In case of acetate and oxalate, the D.T. values for flesh and grain layers are higher to that of control ; but are much lower for middle layer. In all other cases, the values are lower in all layers as compared to the control. The values are lower to that of NaCl system. Further, the D.T. values are far from uniform. The values for grain and flesh layers are very much higher to those obtained for middle layer. This effect is more pronounced in case of formate (67.5 for grain and flesh and 48 for middle layers). The values are fairly uniform throughout the layers in case of lactate and to an extent in case of tartrate and calgon.

(4) NaX + HX system :—Series II : The D.T. values are higher to that of control as well as those obtained in other series. The general trend is to have a high D.T. value for both grain and flesh and a low value for the middle layers. This effect is more pronounced in case of calgon, dichromate and tartrate. The values tend to be uniform throughout the layers only in case of lactate. Same observation is made for this salt in the previous series. Highest values for D.T. were recorded in case of dichromate and formate.

Evidently the single anion used in this system has a beneficial effect in increasing D.T. though it is not uniform throughout the layers. Even in case of calgon and dichromate, the values obtained in Series II are much higher compared to Series I, where the only difference in the system is the presence of NaCl in Series I. Evidently chloride ion is detrimental to the degree of tannage factor.

Recalling the fact that fixed tannin is fairly uniform throughout the layers and the hide substance content is greater in the middle layer as compared to other layers, the trend obtained for D.T. is understandable.

(5) Series III—NaX added to tanliquors : D.T. values are higher as compared to control in all cases except oxalate. The values are much higher particularly in case of citrate, acetate and tartrate. The general trend is the D.T. values for grain and flesh layers are much higher to that of the middle layer as in other series.

(6) As compared to Series I & II, where dichromate was used for treatment of the pelt, the values obtained in Series III where it was added to tanliquor are much lower. This is probably due to the fact that dichromate may precipitate valuable vegetable tannin.

LEATHER SUBSTANCE : (Hide substance + Fixed Tannin)

(1) In the control, the leather substance is higher in the middle layer as compared to other layers. This is only expected because Hide substance value is high in the middle layer and fixed tannin is uniform in all the layers as seen previously.

(2) NaCl + H_2SO_4 system : The trend is the same as observed in control, except the values are considerably higher to that of control. This is due to increase in hide substance values in NaCl system.

(3) NaCl + H_2SO_4 + NaX system : The values are higher to that of control as well as NaCl series in some cases. The values are also more uniform for all the layers particularly in case of calgon, dichromate, acetate, citrate, lactate and tartrate.

(4) NaX + HX system : The values are higher to that of control and equal to or lower to that of Series I above. The values are fairly uniform in case of acetate and tartrate as in Series I.

(5) NaX added to tanliquors : The values in most of the cases are lower to those obtained in Series I & II except in case of citrate. They are very close to control values excepting in citrate and tartrate.

CONCLUSIONS :

1. Certain salts like calgon, sod. acetate, formate, oxalate and citrate tend to increase the speed of penetration of tannin while others like NaCl, sod. dichromate, tartrate and lactate do not have such an effect. The increase in rate of penetration appears to be governed by the concentration of the salt and mode of addition to the pelt or to the tanliquor.

2. All the salts under study did not have a pronounced effect on shrinkage temperature of the final leather. But the study of

shrinkage temperature during the course of tanning confirms the fact that the shrinkage temperature rises with the increase in tannin fixed up to a point and on further increase of fixed tannin, it is lowered and stays constant after that.

3. On physical assessment, the leathers produced using salt systems are equal to and mostly better to that of control in regard to general appearance, solidity, etc.

4. The colour of the leathers is much improved where salts were used and particularly so in case of calgon and acetate series where these salts were used for pre-treatment of the pelt.

5. On stratigraphic analysis, it is observed the middle layers contain more leather content, less water solubles, fixed tannins, oils, D.T. contents as compared to grain and middle layers in case of control experiment. This trend is generally maintained when salts were used for pre-treatment of the pelt or the liquor.

Addition of salts tends to have little or no effect on the distribution or increasing or decreasing in different layers with respect to water solubles, oils and fats and leather contents, whereas an increase is observed in case of degree of tannage, fixed tans.

When the salts are used for pre-treatment of the pelt, an increase in the values for fixed tannins, leather content and degree of tannage and a decrease in the values for water solubles were observed. The pre-treatment with salts tends to increase the penetration of oil into the leather on oiling.

The NaX-HX buffer system appears to be beneficial to obtain higher degree of tannage, uniform fixation of tannin content, whereas NaCl systems are of help to decrease water solubles contents of leathers.

Chem. & Phys. Divn.,
11-6-1956.

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STUDIES ON INSECT DAMAGE TO RAW HIDES -

By larval forms of Anthrenus vorax

R. BHASKARAN, S. N. SEN & PROF. B. M. DAS (LATE).

SUMMARY

Damage caused by the larval stages of *Anthrenus vorax* to stored hides, has been studied and recorded. The damage was restricted to the grain surface of the hide and was of an irreparable nature.

Insect ravages to stored hides, as well as to hides in transit to tanneries, has been the cause of much loss to the leather industry. Line[3], O'Flahearty and Roddy,[4] Belvasky,[1] Stather,[5] and Walker,[6] have described in detail the damages caused, along with the insects responsible for such damages. Recently the authors came across a type of damage caused to flint dried and drysalted hides kept in storage, by the larvel forms of the beetle Anthrenus vorax. This was taken up for a detailed study, as this type of damage appeared to be peculiar, for the damage is restricted to the grain surface, as against the usual type of damage caused by other beetles, which proceeds from the flesh side (O'Flahearty and Roddy loc.cit.).

The larval forms of Anthrenus vorax were encountered on flint dried and drysalted hides that were stored in the laboratory for experimental purposes. These hide pieces were subsequently found damaged and the damages caused could be attributed to these larvi. The affected hide pieces revealed large hairless, denuded patches, with the above larvi at the borders of such areas (refer Fig. 1). The damage was restricted to the hairy surface of the hide, the flesh side being intact. In most cases the larvi were seen at the periphery of such hairless areas, and were encroaching upon fresh areas of attack. The hair and keratin appear to be the chief food of these insects. The larvi gnaw down the hairs to their very roots thereby producing depressions on the grain surface. Around such areas, a large number of moulted larval skins, as well as a much dusty debris constituted by cutdown hairs, as well as the fecal matter of the larvi was present. By progressive activity the larvi gradually extend the area of damage.

On a casual look the damage might appear to be of a superficial nature, but when such hides were examined microscopically and when some representative pieces were tanned and finished the damage proved to be of much greater significance.

Microscopic study :

For the Microscopic study, sections were prepared from samples typical of this damage, with the freezing microtome. The sectional view of the damage is represented in the photomicro-

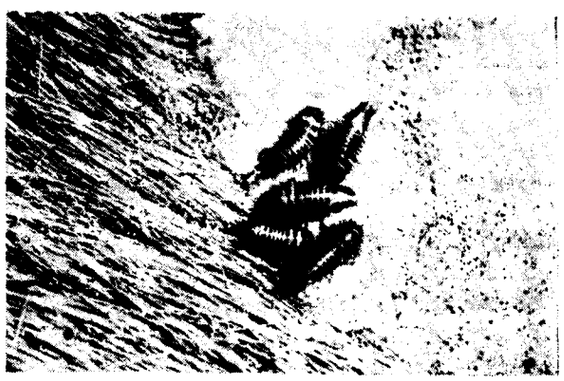

Fig. I.—Photograph of hide piece showing the larval forms of Anthrenus vorax, at the site of damage.

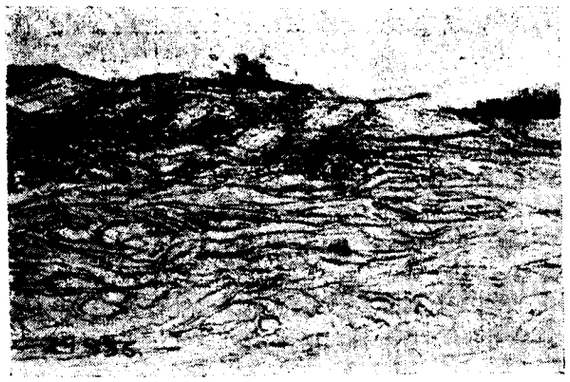

Fig. II.—Sectional view of the damaged hide showing the different layers affected. Magnified about 85 times.

graph (Fig. 2). From this it is evident that the epidermal and grain layers of the hide have been eaten away exposing the corium. In some places the depressions are superficial while in others it might go down to the corium.

An examination of a piece of leather prepared from such pieces, showed badly affected areas on the grain surface. The grain was absent in these areas and instead there were a large number of irregular depressions, giving the leather a rough appearance. It is needless to add that the value of such leathers would be very low.

The Larvi :

These were responsible for the damage. They had a segmented body with three pairs of legs and were hairy and blackish in appearance. The hairs in the last segment were held up in a characteristic manner, resembling a pair of horns. These could be easily maintained on fresh hide pieces, in the laboratory.

Adults :

When the larvi obtained from these damaged hides, were maintained on hide pieces, adults emerged in due course, after a pupal period of about 10 days. Two varieties of adults were obtained, namely, Anthrenus vorax var late basalis, and Anthrenus vorax (waterhouse) respectively. The colour pattern and distribution of the scales on the dorsal surface of these insects, were

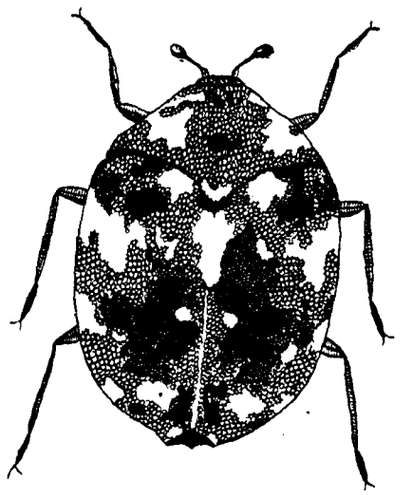

Fig. III.—Dorsal view of Anthernus vorax.

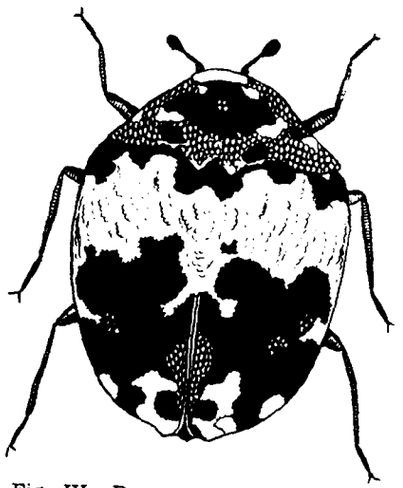

Fig. IV.—Dorsal view of Anthrenus vorax var latebasalis.

identical with those described for them, by Hinton.[2] The dorsal surface of Anthrenus vorax (waterhouse) (Fig. 3) shows a characteristic distribution of coloured scales having a definite

pattern. There are patches of yellowish brown and blackish scales with bands and spots of white ones. In the case of Anthrenus vorax var latebasalis (Fig. 4) the predominating colours are creamy yellow, brown and black with some white coloured patches.

The adults when kept on hide pieces did not cause any damage, similar to those produced by the larvi. Hence it is concluded that only the larvi and not the adults of Anthrenus vorax were responsible for the damage caused to the grain surface of the hide. Further, hides kept in contact with the adults of this species later revealed early larval stages and eggs of this beetle. Thus the adults could account for the damage only in an indirect manner. For further details with regard to the binomics of this species, reference may be made to Hinton.[2]

ACKNOWLEDGEMENT :

Thanks are due to Mr. S. K. Mitra and to Mr. S. C. Nandy for taking some photographs and to Mr. V. A. Lakshmanan, Artist, for drawing the insect from Camera Lucida projections.

Bacteriological lab.

16-10-1956.

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CLASSIFIED ABSTRACTS

RAW MATERIALS

IMPROVED HIDE CURING PRACTICES—*W. Schweisheimer, New York, Aust. Lea. J.* **59**, 3, 136, (1956). : The author deals with the improved hide curing process described by F. L. De Beukelaer of the American Meat Institute Foundation. The operation of brining using the necessary equipments has been described in brief. Brine cured hides are claimed to be superior to the conventional green salted ones from the following points of view. (1) Cure is faster, more uniform and gives greater protection to more adverse conditions, (2) Eliminates salt stains, (3) Soaking back becomes easy and (4) Leather produced will be plumper and has clearer grain.

V.V.S.

THE COLLECTION AND PRESERVATION OF HIDES AND SKINS IN SWEDEN.—*B. Ivarsson & Fredholm. Das Leder,* 1956, 7, 79. *Via. J.S.L.T.C.* **40**, 9, 311, (1956) : Leather from brined hides was softer, lighter in colour, and less veiny ; brined hides were cheaper to ship as their gross weight is lower than that of salted hides. The rate at which salt is taken up by the skin is dependent upon the time elapsing between flaying and salting : when this period is 1 hour, the salt uptake is reduced by 30%—after 6 hr., the reduction is about 75%. Bacterial effect is also increased by delay in salting. Tests with the APC method of curing with impregnated paper have confirmed German results that it is satisfactory and gives a higher leather yield than do the usual methods : the APC method is dearer and more difficult to apply. Salt spots were always associated with the presence of soluble salts of calcium or magnesium : when such salts were excluded, salt spots did not appear. It is not sufficient to exclude Ca and Mg from the curing salt, they must not gain access through water. On examining samples of water from slaughterhouses, the occurrence of Ca and Mg salts and of salt spots on skins were found to be interrelated. Hard water is no longer used for washing freshly flayed skins. Calf skins exhibited veininess : research showed that this was related to the temperature at which the skins were stored after flaying. Skins rapidly cooled after flaying seldom showed veininess.

A SURVEY OF SKIN DISEASES OF GOATS IN KENYA AND THEIR EFFECT ON THE FINISHED LEATHER.—*H. F. Green. J.S.L.T.C.* **40**, 8, 259, (1956) : The diseases are described and illustrated as they appeared on the dry raw skins, in sections through lesions and on the finished leather. Demodicosis and streptothricosis were the most prevalent and the most damaging to the leather. Two unidentified diseases, which have been named "scurf" and "dimple," were next in order of prevalence. "Scurf" has very little adverse effect on the leather. Sarcoptic mange is relatively uncommon. A similar survey of cattle hides is being undertaken.

N.S.

IMPROVED TECHNIQUE FOR STAINING RED HALOPHILIC BACTERIA.—*H. P. Dussault. J. Bact.* 1955, 70, 484 ; *Stain Technol.*, 1956, 31, 99. *Via. J.S.L.T.C.* **40**, 8, 273, (1956) : A method is proposed in which red halophilic bacteria from salted hides or fish are suspended in sterile 20% brine which is mixed thoroughly to break up slime ; this is spread on a clean slide, air dried, fixed and desalted by immersion in 2% acetic acid for 5 min., dried unwashed, and stained with 0.25% aqueous Crystal Violet or a Gram stain.

COMPARATIVE TESTS OF THE EFFECTIVENESS OF DDT AND BHC DUSTING POWDERS AGAINST THE "HIDE OR LEATHER BEETLE," DERMESTES MACULATUS DEGEER (COL. DERMESTIDAE).—*Gwyneth C. Williams. J.S.L.T.C.*, **40**, 8, 253, (1956) : Laboratory tests indicate that BHC applied in the form of dusting powder containing 5% gama-isomer will control *Dermestes Maculatus* successfully both in adult and larvae stages whereas DDT applied as 5% dusting powder affects the adults only and is slower in producing toxic symptoms. The larvae of D. maculatus react more slowly to BHC than the adults but become moribund within 24 hours and will remain in this state for more than 72 hours before dying. The effective dose of BHC appears to be picked up while larvae are still able to walk on the insecticide and fumigant action seems to play no noticeable part in hastening death once the moribund state is reached. DDT is inaffective against larvae of D. maculatus.

N.S.

SOME NOTES UPON LEATHER QUALITY AND HIDE QUALITY.—*Raymond Hauck and Robert M. Lollar. Via. Shoe & Lea. Rep.* **283**, 1, 25, (1956) : Tanners generally agree that the production of good quality leather is dependent upon satisfactory quality in cured hides. However, their current methods of assessment of hide quality are largely dependent on subjective quality indicators. The literature contains but few reports of practical attempts to assess the relationship between cure quality and potential leather quality. Further, most of this available information in concerned with vegetable tanned sole leather.

Objective methods of assessment of cure quality might include estimation of the moisture, salt and leather-making-substance content of the hide lots, along with examination of the hide lot samples for content of volatile nitrogen, free fatty acids, and micro-organisms. However, the validity of such assessment methods would have to be established by pilot scale studies.

This paper presented a review of the literature which is concerned with this subject. Further, preliminary experiments including the production of pilot scale lots of side leather were reported. These experiments have involved the comparison of correctly cured hides to hides cured after excessive delay of cure, so as to determine the relation between the level of cure and the resultant leather quality, which will enable specifications for good quality cured hides to be written. This preliminary report was presented in the hope that it will stimulate further work in this important field.

PROCESSES PRIOR TO TANNING

THE SOAKING OF DRIED LIGHT HIDES FOR FULL-CHROME SIDE LEATHER.—*M. Dempsey. J.S.L.T.C.* **40**, 9, 287, (1956) : Hides were treated in water, then salt solution to which, later, sulphide was added. They were drummed a little after the water treatment, but only turned over several times during the rest of the soaking, and were washed and green fleshed before liming. Of the five tanneries co-operating in the trials, two reported that the resultant leather was too soft, one that it was a little mellower than their usual production, and two that it was satisfactory. These results are to be related to the vigour of the processes subsequent to soaking in the different tanneries : where the usual soaking was, like the experimental soaking, thorough, the associated processes had been already adapted to this and over-opening up of the fibre structure was thus avoided. One of the tanneries carried out the further experiment of halving its usual time of liming after the experimental soaking and thereby produced a very satisfactory leather better than the usual production. These results, though encouraging, should not be regarded as final. Leather softer than that from wet-salted hides has been produced by opening up dry hides by chemical means and a very little mechanical action, and strong subsequent treatments. Cutting down the liming has resulted in a leather of good quality for dry hides. It should be possible now, in the light of this experience, to investigate further the production from dry hides of leather more nearly approaching that from wet-salted hides.

MODERN TRENDS IN FELLMONGERING.—*P. T. Brown. Wool (N. Z.)*, 1955, 2, (3), *pp.* 31-35. *Via. J. Tex. Inst.* **47**, 2, 65, (1956) : The increase in the number of sheep coming from the farms to the freezing works, that has necessitated the introduction of the chain system of killing, has also brought problems in the fellmongering departments. As the average value of a skin may be 25-30 per cent of the live value of the sheep, it is important that these problems be solved. Some of the ways of speeding the process of depilating (painting method) that have been tried are described.

BEAMHOUSE PROBLEMS IN THE MANUFACTURE OF LIGHT LEATHER.—*G. Walther. Das Leder*, 1956, 7, 1. *Via. J.S.L.T.C.* **40**, 9, 310, 1956) : Dried or dry-salted goat skins should be broken over during soaking : addition to the soak is often made of sodium hydroxide, sulphide, or tetrasulphide. Soaking in formic acid solution increases water uptake but causes loose grain : a solution of common salt gives satisfactory results. The use of surface-active agents in soaking offers no advantages in accelerating water uptake, but helps in removing grease if accompanied by movement of the liquor.

Dried sheep skins cannot be drummed on account of felting of the wool, but breaking over can be done. Enzyme unhairing of goat skins is carried out successfully in Germany after modification of their original Ara process. It requires careful sorting of the skins according to area and thickness. Emulsifying agents in the lines do not increase fat removed from sheep skin. Degreasing of pickled goat pelt with trichlo-

roethylene reduces fatty spue but salt patches still occur which are described to the Khari salt used in curing. Recent tests have shown the presence of 4-21% magnesium sulphate in Asiatic curing salt. Synthetic bates have not given such good results as dog dung in treating goat skins.

ATMOSPHERIC OXIDATION OF ALKALI SULPHIDE SOLUTIONS AND ITS EFFECT ON THE UNHAIRING AND DEWOOLLING OF SKINS.—*Henry Booth. J.S.L.T.C.* **40**, 7, 226, (1956) : Alkali sulphide solutions are oxidised by air by two different mechanisms : (1) in less alkaline solutions NaHS or $(NH_4)_2S$ with limited oxygen supply—polysulphide formation ; (2) With good aeration or more alkaline solutions, a reaction catalysed by iron. Reaction (1) is slow, complete oxidation taking a few days or weeks. Reaction (2) can be extremely rapid in alkaline solution with good aeration or on a surface where access of air is easy, complete oxidation taking less than a day. The ultimate products of both are normally thiosulphate, but with reaction (2) in alkaline solution one-third of the sulphide can be oxidised to sulphite if there is a restricted supply of oxygen.

An account is given of the mechanism of the catalytic oxidation, which involves the formation of ferric sulphide, the ferric salt of a complex anion $(FeS_3)\cdots$. Some of the iron can be present as complex sulphides which are without catalytic action. The consequences of the oxidation of sodium sulphide in the presence of lime by the iron present in all types of skin are discussed.

STUDIES ON ENZYMES FOR LEATHER MANUFACTURE : PART I. FACTORS INFLUENCING THE FORMATION OF PROTEOLYTIC ENZYMES IN CERTAIN MOLDS.—*S. M. Bose, S. C. Dhar and B. M. Das. Tanner,* **11**, 2, 17, (1956) *and Tanner,* **11**, 3, 27, (1956) : 1. Proteolytic activity of 4 strains of molds A. parasiticus, A. oryzae, A. flavus and A. niger were comparatively studied. A. parasiticus was found to give the highest proteolytic activity.

2. The influence of several cultural conditions, viz., incubation period and temperature, pH of medium, age and amount of inoculum, aeration and depth of medium, on the production of proteases by A. parasiticus was systematically investigated. The maximum concentration of the enzymes was obtained when the culture medium of pH 6 was incubated at 33°C for a period of six days. Aeration of the culture medium was found to increase the protease production considerably.

3. The important nutritional factors which affect the production of proteases by A. parasiticus were critically investigated. These were the effects of different carbohydrates, different forms of organic and inorganic nitrogen, ratio of protein to carbohydrate and different metallic salts in the culture medium. The results obtained have been discussed with reference to the effect of each factor studied. The presence of 4.0% sucrose and 4.0% peptone in the culture medium was found to be quite effective for the greater production of mold proteases. The addition of metallic salts to the medium resulted in significantly greater production of proteases.

4. Based on the results obtained, the composition of a medium for the maximum production of proteases by A. parasiticus has been suggested.

CHROME TANNING

REDUCTION OF CHROMIC ACID IN SOLUTION IN SULPHURIC ACID BY NATURAL AMINO-ACIDS.—*Garcia-Blanco, J. and Pascual-Leone, A.M. Rev. espanola Fisiol.,* 1955, 11, 143-147. (*Lab. Fisiol. Gen., Fac. Med., Valencia*). *Via. Nut. Absts. & Rev.* **26**, 2, 310, (1956) : The amino-acids were dissolved in water or HCl solution. The test solution was prepared by slow addition of I ml. 0.5N or 0.25N potassium chromate to 20 ml. concentrated H_2SO_4, and 1 ml. of this was added immediately to 1 ml. amino-acid solution, in a boiling-water bath. The reduction of yellow chromate to blue-green indicates the end-point of the reaction. The smallest amount of amino-acid capable of reducing the potassium chromate in 10 min. was found.

The concentrations of amino-acid necessary, in mg. per ml., were *iso*leucine 0.125, leucine, tyrosine, lysine and serine 0.185, arginine 0.25, cystine, cysteine and valine 0.375, phenylalanine and methionine 0.5, histidine I, proline 2, asparatic and glutamic acids 60, alanine 100 and glycine 200.

ANALYSIS OF COMPLEX CHROMIUM IONS BY ELECTROPHORESIS : QUALITATIVE AND QUANTITATIVE ANALYSIS.—*A. Kawamura, H. Okamura, and N. Naneko. Japan. Analyst.,* 1955, 4, 158 ; *Analyt. Abst.,* 1956, 3, *No.* 97. *Via. J.S.L.T.C.* **40**, 8, 274, (1956) : When developed with N/30 NC104, the spots of oxalto-chromium ions are separated electrophoretically without significant decomposition. Mobilities of chromium complexes containing NH_3, SCN, SO_4, and OH groups are practically identical with those of the oxalate complexes having the same charge. When a chrome tanning liquor, obtained by the reduction of dichromate with various reducing agents, e.g., glucose, methanol, glycerol, ethanediol, and thiosulphate, is examined by this method, several spots are observed corresponding to differently charged chromium complexes. Charges depend on reducing agent used, and on concentration of neutral salts in the dichromate solution. The electrophoretic spots of chromium of different charge are so clearly separated that the paper can be cut and chromium extracted from the spots for analysis.

VEGETABLE TANNING

VEGETABLE TANNING MATERIALS OF U.P.—R.K. *Agarwal & G. D. Pande. Tanner,* **11**, 3, 13, (1956) : With a view to get over the shortage of tanning materials keenly felt by the Indian tanning industry, the authors have suggested nearly 36 tanning materials available in U.P. that have been tried and could be used to the best advantage. Further there are about 10 other materials containing a fairly good percentage of tanning which needs investigation as to their availability as well as the possibility of manufacturing extracts.

KAHWA BARK IN SOLE LEATHER MANUFACTURE.—*P. V. R. Krishna Reddy, K. A. Joseph and K. Padmanabhan. .Tanner,* **11**, 4, 21, (1956) : The production of sole leather in the Madras State is not commensurate with the production of buffalo hides in Madras mainly due to the shortage of the widely used tanning materials. A study on this was made with a view to know the suitability and utility of the indigenous Kahwa bark which contains about 20% tannin. The practical tanning trials conducted have revealed that Kahwa bark when used alone gives a 63% degree of tannage and the leather produced is reddish in colour and the grain cracky. But when a blend of Kahwa and Myrab in the ratio of 1 : 1 yielded leather with 81% degree of tannage and the quality of leather produced satisfied all the necessary specifications and qualities.

A NEW SUBSTITUTE FOR IMPORTED WATTLE BARK.—*P. V. R. Krishna Reddy, K. A. Joseph and K. Padmanabhan. .Tanner,* **11**, 4, 23, (1956) : The Indian tanning industry has realised the unfortunate position of depending on foreign imported tanning material and there is a vigorous drive all round to find newer substitutes for wattle bark and extract from out of the indigenous sources. Cassia Siamea, an indigenous material, was investigated and it is found to contain about 23% tannin. The bark contains easily extractable tannins and the yield of leather is higher than in the case of leather tanned with wattle bark. This bark may prove a promising substitute for wattle bark in the tanning of E. I. kips.

THE USE OF HIDE-POWDER ANALYSES FOR EVALUATING THE TANNIN BALANCE IN VEGETABLE TANNING.—*P. J. van Vlimmeren, J.S.L.T.C.* **40**, 8, 265, (1956) : A method is described for drawing up a tannin balance in vegetable tanning. Pelt and chromed hide powder give the same results, but hide powder is preferred for convenience. Either the shake or filter-bell methods can be applied. For used liquors containing excessive semi-and non-tannins, the analytical solution must be of the prescribed strength to avoid misleading results. The N x 5.62 factor for hide substance (or other factor established) is not correct for tanned leather. Water of hydration is displaced by the vegetable tannins and the factor reduced to an extent depending on the intensity of tannage.

SOME RELATIONSHIP BETWEEN WATER UPTAKE OF PELT AND TANNIN FIXATION.—*G. Cooper and R. B. Newton. J.S.L.T.C.* **40**, 9, 279, (1956) : The amount of fixation of material from a vegetable tanning liquor is proportional to the water uptake of the pelt from these liquors prior to tannage. Different acid/salt systems have been studied, and while for each system this holds true, there is a different numerical relationship between water uptake and degree of tanning for each system.

Providing the pK value of the acid at each ionisation level is greater than that of collagen the valency of the anion will determine the water uptake level. The valency of the cation has no effect on the water uptake level, but each has its own specific effect.

SPECIAL CHESTNUT EXTRACTS.—*P. Peureux. Rev. tech. Industr. Cuir,* 1955, 47, 188. *Via. J.S.L.T.C., No.* 7,242, (1956). A survey of the changes in the use of chestnut extracts during the last twenty years. Improvement of extracts since sweetening was introduced in about 1930 is discussed. The pH of "Special Extracts" can be adjusted without altering their astringence to give leather with improved properties.

PROCESSES AFTER TANNING

SYNTHETIC LEATHER OILS.—*W. Pense. Das Leder,* 1956, 7, 29. *Via. J.S.L.T.C.* **40**, 9, 311, (1956) : Chlorinated hydrocarbons are not subject to drawbacks associated with glycerides and mineral oils. The properties of a series of chlorinated straight-chain hydrocarbons from C_{14} to C_{24} are given. Curves show the relationship between chlorine content and viscosity and density. These products easily form emulsions with water and prevent mould growth. Fats solubilised by reaction with polyethylene oxide are incompletely fixed by leather ; they are of value as accessory agents and increase the wettability of chrome-tanned leather. A new class of materials is the sulphamido acetic acid salts ; the properties of the oil depend upon the length of the hydrocarbon chain.

DYES USED IN LEATHER COLOURING.—*Joseph A. Casnocha. Shoe and Leather Rep.* **281**, 9, 16, (1956) : Coloring the correct dyestuff out of a few hundred of synthetic dyestuffs in the market presents a problem for the tanner as colouring is an intricate process and the reactions involved delicate due to the complex nature of the dyestuffs. Though each dyestuff differs from the other, some way or other, a general classification has been done on three broad heads, viz. anionic, cationic or basic and fast colour groups. The dyes ordinarily known as acid, direct and chrome dyes belong to the anionic group. The second group which less numerous, includes all the basic dyes which contain positive charges. To the third group known as fast colours belong sulphur ores, wat dyes, naphthal dyes etc. All the three groups are separately dealt with by the author.

V.V.S.

APPROACH TO COLOUR MATCHING:—*R. H. Leach. Shoe and Leather Rep.* **281**, 9, 14, (1956) : Different factors that affect the matching of a particular shade in dyeing of leathers are, cost, water conditions, types of tannages, pH of leather, effect of syntan in tanning and dyeing operation, shade to be finished and whether aniline effect is desired, selection of the dyes, effect of organic acids in exhaustion of dyebaths, washing of the dyed leathers, effect of fatliquors and finally the drying condition of the leather. Effect of all these factors have been discussed in brief. A procedure in which a dye technician should proceed to colour matching is given.

Some aspects of colouring, fatliquoring and drying of leather in order to obtain a uniform shade are also been dealt with by the author.

V.V.S.

COVERING POWER OF PIGMENTS IN LEATHER FINISHING.—*E. Belavsky and T. Termingnoni. Rev. Quim. Industr., Rio de Janeira,* 1955, 24, 21 ; *J. appl. Chem. Abs.,* 1955, *ii,* 824. *Via. J.S.L.T.C.* , 7, 244, (1956) : For good finishes, particle size of the pigment must be

less than the thickness of the film, and pigment must be air-and light-fast. Covering power depends on the comparative refractive indices of pigment and medium. Three general bases are used for leather finishing : casein, nitrocellulose, and polyacrylic or polyvinyl resins. Tests were made using a number of combinations of medium and pigment. Titanium oxide with its high refractive index (2.30—2.46) has high covering power in all media, especially synthetic resins, and may be cheapened by mixing with barium sulphate. A table gives pigments and media for leather finishes of various colours.

THEORIES

CHANGES IN FIBRE STRUCTURE OF HIDE DURING THE MANUFACTURE OF CHROME SIDE UPPER LEATHER.—*M. Dempsey. J.S.L.T.C.* **40**, 9, 298, (1956) : The changes in fibre structure of wet-salted and of dried hides have been followed in several tanneries. The observations recorded suggest that opening up of the hide continues throughout the wet processes up to the fat-liquored stage, and hence maximum opening up at the end of liming should not be aimed at. However, under-opening up of dry hide in the limed stage led in one tannery to excessive staking, in which the fibre bundles were broken to soften the leather. On drying, the chromed fibres re-stick, but after staking the structure is, to a limited extent, re-opened. Drying the leather under tension lowers the angle of weave.

The relation between raw hide and finished leather was well illustrated. Dry hides were normally more compact than wet-salted through the process, and the finished leather made from them was stiffer and stronger (tensile and buckle tear tests). Bacterial degradation in the raw hide led to loose structure during the process and weak grain in the finished leather.

ON THE REACTION BETWEEN UREA AND FORMALDEHYDE IN NEUTRAL AND ALKALINE SOLUTIONS. I. EXPERIMENTAL STUDIES OF THE RATES OF THE EQUIMOLECULAR REACTION.—*Nils Landqvist. Acta Chem. Scand.*, 1955, 9, *No.* 7, *pp.* 1127-1142. *Via. J. Text. Inst.* **47**, 3, *A*150, 1956 : Some methods for determining formaldehyde in urea-formaldehyde reaction solutions are examined. A number of effects which have to be considered when applying polarography to this system are analysed and a suitable supporting electrolyte composition is given. The results are presented of reaction rate studies at 20°C of the equimolecular reaction between urea and formaldehyde at comparatively high concentrations of the reactants.

SPECTROPHOTOMETRIC STUDIES ON METAL-DYE COMPLEXES. I. THE REACTION BETWEEN SOLOCHROME VIOLET RS (2-HYDROXY-5-SULPHOPHENYLAZONAPHTHOL) AND TERVALENT CHROMIUM.—*R. B. Bentley and J. P. Elder. J. Soc. Dyers & Col.* **72**, 7, 332, (1956) : An investigation has been made by spectrophotometric and chromatographic methods of the reaction between an oo'-dihydroxyazo dye and tervalent chromium salts. The two complexes formed have been separated chromatographically and their spectra measured. Equilibrium constants for the interconversion of the two

complexes have been determined, together with the heat, free energy, and entropy changes for this reaction.

SWELLING OF PROTEIN MOLECULES IN SOLUTION.—*T. L. Hill. J. Phys. Chem.*, **60**, 358-361 (*March* 1956). *Via. J. Soc. Dyers and Col.* **72**, 7, 366, (1956) : The suggestion of Yang and Foster that serum albumin swells at low pH because of an $\alpha \rightarrow \beta$ tranformation is examined theoretically, and the mechanism suggested is found to be a reasonable possibility. The theory, however, predicts a salt effect opposite in sign to that found experimentally.

FIBRE SCIENCE AND LEATHER SCIENCE.—*H. Phillips. Chim. et Ind.*, 75, 263-274 (*Feb.* 1956) : *Rev. Tech. Ind. Cuir*, 48, 111-124 (*June* 1956). *Via. J. Soc. Dyers & Col.* **72**, 8, 405, (1956) : The chemical constitution and the physical structure of collagen are reviewed : the fibrous character of collagen is emphasised, and analogies with common textile fibres are drawn. Evidence of alternating regions of crystallinity and amorphousness in collagen fibrils is reviewed ; the crystalline regions are " autoprotected ", whilst the amorphous regions are protected and reinforced by tannage. The degree of crystallinity of collagen may be determined either (1) from the sorption isothern, (Hailwood and Horrobin, Trans. Faraday Soc., 42, 84 (1946), or (2) by deuteration (method of Hill and the author) through prolonged exposure to D_2O vapour, the labile hydrogen of peptide, amino, guanidyl, amido, and carboxyl groups being replaced by D. The latter method gives much lower values than the former ; the difference is serious, but attention is drawn to the complexity, sensitivity, and the importance of the history of the fibrous system concerned. The action of tannage upon the amorphous regions of the fibres occurs in two stages—(1) association between the tannins and the exposed molecular chains of collagen ; (2) association between the fixed tannins and further tannin molecules, which continues until all the accessible free space is occupied. At this stage tannage is complete, and 100 parts of fibre retain 50 parts of tannin. Measurements of the rate of tannage with 10 different tannins [Stather and Lauffmann, Collegium, 78G, 420 (1935)] have shown that tannage is virtually complete within 22 days. Roddy [J. Amer. Leather Chem. Assocn. 38, 143 (1943)] has effected complete tannage within 48 hr. by means of a conc. soln. of quebrache in acetone followed by fixation of the tannin by steeping in water, or in a soln. containing H_2SO_4 (1%) and NaCl (10%), in each case for 24 hr. The resulting degree of tannage (47-48) was increased (to 70-80) by subsequent tannage in the works. Pretannage liming causes slow separation of the molecular chains in the amorphous regions of the collagen, thus increasing the " Water-soluble " tannin [that removable from the tanned leather by a prolonged extraction with water, corresponding to a stage (2) above] ; the fixed tannin [that which resists water extraction, corresponding to stage (1) above] is virtually unaffected, showing that no opening up of the cryst. regions occurs. Tannage in weak acid soln. at an elevated temp. (" hot-pitting ") swells the amorphous regions, and even opens up the cryst. regions to a small extent ; this method gives hard and impermeable leathers suitable for soling. Modification of the cryst. regions must be minimised to avoid weakening the leather.

A STUDY OF THE PHOTOCHEMISTRY OF DYES ON PROTEINS AND OTHER SUBSTRATES—*J. W. Cumming, C. H. Giles and Miss A. E. McEachran... J. Soc. Dyers & Col.* **72**, 8, 373, (1956) : The rates of oxidation and of reduction in aqueous solution, and of fading in films of a typical protein (gelatin) and a typical non-protein (methylethylcellulose), have been determined for several series of dyes of different chemical classes. The general conclusion reached is that the photodegradation of a dye may follow either of the alternative mechanisms of oxidation or reduction, but normally oxidation occurs more readily on all non-proteins and reduction of proteins. In photochemical oxidation of dyes of non-proteins the substrate does not necessarily take part directly, but in reduction on proteins some constituent of the protein itself appears to act as the reducing agent. The histidine side-chains are probably the active constituent.

The conclusions in some instances have been confirmed by examination of spectral absorption curves of oxidation, reduction, and fading products of certain dyes.

THE INFLUENCE OF HISTOLOGICAL FACTORS ON THE ATTACK OF THE WOOL FIBRE BY VARIOUS REAGENTS—*R. L. Elliot and J. B. Roberts. J. Soc. Dyers & Col.* **72**, 8, 370, (1956) : An investigation including optical and electron microscope studies, of the sequence of attack of various reagents on wool has revealed significant variations in the stability of the histological components of the fibre. In particular, further information has been obtained about the resistant membranes, together with additional evidence of a tubular resistant membrane lying immediately beneath the cuticular layer, and completely surrounding the cortex. This membrane is identified with the subcuticular membrane of Alexander and Earland. The lability of the orthocortex, and the greater stability of the paracortex, towards hydrolytic reagents, have also been confirmed. Observations on the action of oxidising agents, such as N-chlorourea and acid potassium permanganate, are also included. Details are given of a new rapid technique for obtaining fibre replicas for electron-microscopic examination.

TESTING

PROPOSED OFFICIAL METHODS FOR THE DETERMINATION OF THE ACIDITY OF VEGETABLE TANNED LEATHER—*D. Burton. J.S.L.T.C.*, **40**, 8, 245, (1956) : Proposed official method for the determination of the acidity of vegetable tanned leather is described.

PROPOSED OFFICIAL METHOD FOR THE DETERMINATION OF THE NEUTRALISATION VALUE (BUFFER CAPACITY) OF VEGETABLE TANNED LEATHER—*D. Burton, J.S.L.T.C.*, **40**, 8, 248, (1956) : Proposed official method for the determination of the neutralisation value of vegetable tanned leather is described.

PROPOSED OFFICIAL METHODS FOR THE ANALYSIS OF SULPHATED OILS—*D. Burton, G. F. Robertshaw and C. H. Pearson. J.S.L.T.C.*, **40**, 8, 248, (1956) : Proposed official method for the analysis

of sulphated oils is described. The methods for the determination of pH, ash, acid value, unsaponfiable matter, total alkalinity, organically combind SO_3 existing as neutralised sulphuric esters, organically combined SO_3 existing as neutralised sulphonic acid groups, inorganic sulphates and chlorides are described.

QUANTITATIVE TANNIN ANALYSIS AND HIDE POWDER COMMITTEE—*J. P. Danby. J.S.L.T.C.*, **40**, 8, 253, (1956) : The method is described for use in determining the pH of vegetable tannin extracts and tannery liquors by means of glass electrodes using a normal set up or a reliable pH meter. This is an addition to the proposed official methods.

FURTHER TESTS IN IMPROVING THE RESISTANCE OF INSOLES TO PERSPIRATION—*W. Grassmann and P. Stadler. Das Leder*, 1956, 7, 8. *Via. J.S.L.T.C.*, **40**, 9, 309, (1956) : An after-tannage with a cationic syntan increases the resistance to perspiration of insole leather tanned solely with syntans. Tannage solely with sulphite cellulose extracts confers little resistance to perspiration ; such resistance is increased by an after-tannage with resin tannins (melamin or dicyandiamide) shows high resistance to deterioration through perspiration. When using a cationic tannage, the leather should be washed well to free it from excess syntan or vegetable tannin. The final leather shows no reduction in desired physical properties compared with the original material ; the watersolubles are considerably reduced by the treatment. Insoles of reconstituted leatherboard behave differently towards synthetic alkaline perspiration depending on whether they are of chrome or vegetable fibre. Their change in area on wetting and drying varies considerably among the various makes ; none became hard on wetting and drying.

WEAR TRIALS OF SOLE LEATHER—*P. Chambard. Bull. A.F.C.I.C.*, 1955, 17, 248. *Via. J.S.L.T.C.*, **40**, 8, 274, (1956). Wear coefficients (calculated as the number of km. necessary to wear through 1 mm. leather) are similar to results from abrasion tests, but owing to wide differences between results from different wearers, it is difficult to predict wear from abrasion tests. Results so far show that chrome retan is superior to other leathers tested ; absence of water-solubles, and porosity which aid elimination of perspiration, increase comfort in wear. Trials are continuing.

DETERMINATION OF VOLATILE OIL IN EFFLUENTS—*J. G. Sherratt. The Analyst*, **81**, 966, 518, (1956) : An account is given of a method for determining traces of neutral volatile oils, such as fuel oils, in waters and effluents. The solubility of certain types of fuel oil in water is considered, and some of the effects of pollution of natural waters by oil are briefly described.

THE AMINO-ACID COMPOSITION OF KERATINS. III. THE AMINO-ACID COMPOSITION OF DIFFERENT QUALITIES OF WOOL —*D. H. Simmonds. Aust. J. Biol. Sci.*, 1955, 8, pp. 537-540. *Via. J. Tex. Inst.*, **47**, 4, A200, (1956) : Using the analytical procedures described in the first parts of the series (J. Text. Inst., 1954, 45, A511 ; ibid., 1955, 46, A622), the amino-acid composition of Merino 7^{os} and Corriedale 5^{6s} wools

have been determined and the results compared with those previously obtained from Merino 64^s quality wool. Only small (maximum 25% ; majority under 10%) variations in amino-acid contents occurred among the three qualities.

THE GROSSE-BOHLE-CHAMBARD REACTION FOR TESTING FOR FORMALDEHYDE—TANNED CHAMOIS.—*R. Airoldi, Cuoio, Pelli Mater. Concianti,* 1955, 31, 147. *Via. J.S.L.T.C.* **40**, 8, 275, (1956) : The Grosse-Bohle-Chambard method for testing for formaldehyde has been investigated as a result of doubts as to its effectiveness. The method, which is described in detail, is found not to be absolutely typical, but among tanning materials may be regarded as specific for mormaldehyde. The reagent does not identify formaldehyde in leather two years old or more, nor in leather treated with less than 0.5% formaldehyde. By decoloration with active carbon before testing, formaldehyde may be detected in dyed chamois. The test also gives good results in the detection of formaldehyde used as a fixative in water-pigment finishing, in samples less than two years old.

FRACTIONATION OF BASIC PROTEINS AND POLYPEPTIDES.—*F. S. Scanes and B. T. Tozer. The Biochem. J.* **63**, 4, 565, (1956) : The application of the techniques elution of chromatography from basic alumina and counter-current distribution to a commercial sample of *clupein* and of *salamine* led to the partial separation and identification of their components. A modified Sakaguchi-Weber method of determination of arginine was used for the assay of whole clupein in the samples obtained on fractionation. The solvent system for the counter current distribution was n-propanol and a conc. salt solution and chromatographic separation was done by elution from basic alumina. The amino acid composition of clupeins was determined by starch chromatography of the acid hydrolystes, and the N-terminol amino-acids were determined by paper chromatography of hydrolysates of the DNP (dinitrophenyl) derivatives. Crude clupeine has been shown to contain three main components Y1, Y2 and Z and a number of minor components. Clupein Z showed the simplest amino-acid pattern with alamine as the N-terminol amino acid, whereas the other clupeins have alanine or proline as the N-terminol amino acid. The elution and counter current distribution patterns of salamine were qualitatively the same as those of clupeine.

G.R.C.

GENERAL

SKIN TROUBLES FROM WEARING LEATHER GOODS, GLOVE, SHOES, HATBANDS, POCKET BOOKS — AS TROBULE-MAKERS.—*Dr. W. Schweisheimer, New York. Aust. Lea. J.* **59**, 4, 81, (1956) : In his paper, the author has elaborately discussed the various causes of dermatitis in leather goods handling and shoe-wearing. He has reviewed the inferences drawn by the famous skin-trouble experts Dr. Louis Schwartz and Dr. S. M. Peck. According to them the following may be the causes of the skin troubles. Dyes : Bismark brown ; amindo-azobenzene ; amino-azo-toluena by-dorchloride, chrysoidine. Tanning agents : Chromates, oak, sumac, quercitron. Finishes : Fish oil, castor oil, resins. Mildew proofing agents : Marcaptobenzothiozol, tatrabrom

orthocresol, paranitrophenol, pentachlorophenol, salicyl analid and dihydroxy dichlor diphenyl methane. The causes of skin irritation from shoe polishes and artifical leathers have also been discussed.

S.M.D.

FORMATION OF FACTICE AS A CAUSE OF SPUE ON LEATHER.—*F. Stather and G. Konigfeld. Das Leder,* 1956, 7, 35. *Via. J.S.L.T.C.* **40**, 9, 311, (1956) : In a number of cases, particularly with russet upper leather, small spots of exuded material appear on the flesh or grain. The spots are usually round, light to dark brown, and irregularly placed : at first sight they resemble gummy spue, but they are not sticky and are rubbery in feel. When heated, the exudation does not behave like gummy spue but melts with decomposition : it does not dissolve in any of the usual solvents, and gives a strongly positive reaction for sulphur. From this and other evidence it is concluded that factice has been formed. Factice is a rubbery material formed by heating unsaturated oils with sulphur or sulphur chloride. The leather which exhibited the exudation had been made by treating the pickled pelt with sodium thiosulphate before tannage ; later, it was stuffed with a tallow-sod oil cod oil mixture, bleached with oxalic acid, and finally neutralised with thiosulphate. The exudation had sp. gr. 1.03 and contained 1.7% sulphur.

WHAT IS AHEAD FOR LEATHER IN THE AUTOMOTIVE INDUSTRY.—*Fred O' Flaherty, William T. Roddy and Robert M. Lollar. The Lea. Manf.* **73**, 9, 27, (1956) : It is estimated that one million pounds of chemicals are used per year by the total leather industry. Upholstery leather would use a substantial portion of the total amount. Approximately 200 million pounds of chemicals a year go into the manufacture of leather for the automobile industry. In the past the chemicals used by the manufacturer of automotive upholstery leathers have been chiefly heavy chemicals and vegetable tannins with smaller amounts of pigments, lacquers, resins, and plasticizers used in finishing the leather.

The three dimensional weave of cattle hide is chemically stabilized in the production of upholstery leather by the use of natural vegetable tannins. The unique surface texture of the final leather is protected by use of nitrocellulose or ethylene derivative finish coats to produce a superior wearing and tear resistant fabric with long serviceability in the automobile industry.

Current research in the leather industry foretells a revolution in the tanning of hides. Since time immemorial the tanning industry has used water as the solvent for the tannins, but to-day research has developed organic solvent processing systems. These systems will give the tanner much greater versatality in the use of chemicals which could be employed in the production of leather. Therefore, the upholstery tanning industry will become an even greater consumer of many chemicals than it is currently.

Already new leather types are being seen such as those with greater color variety or novel upholstery with new surface effects. This change in production will cause shifts in the consumption of chemicals such as dyes, pigments, and finish components.

Minor uses of leather in the automative industry include gasket and oil seal leathers. In the future it seems possible that the emphasis for safety will include leather on the instrument panel and leather safety belts to hold the occupants in their seats during unusual impact.

The unique properties of leather, especially its high tensile strength and its excellent resistance to flexural fatigue, ideally suits it to the special uses which continuing automotive design will develop. Future chemical research and development gives promise of new and novel leather characteristics which will greatly enhance the future styling of automobiles.

BY-PRODUCTS

THE MANUFACTURE OF GELATINE.—*Albert Rousselot. Chem. et Industr.*, 1955, 74, *No.* 4, *pp.* 669-680. *Via. J. Text. Inst.* **74**, 3, A149, *(1956)* : The raw materials are reviewed and a short description is given of various phases of industrial gelatine preparation. Methods of control are also mentioned, and the importance of gelatine and its uses, particularly in the food industry, are pointed out.

PATENTS

DRYING HIDES OR SKINS.—*British United Shoe Machinery Co BP* 750,416. *Via. J. Soc. Dyers & Col.* **72**, 9, 466, (1956) : The hide is placed between a heated rubber sheet and a porous plate, suction being then applied to the side of the plate away from the hide. This prevents shrinkage during drying.

DICYANDIAMIDE-FORMALDEHYDE RESINS FOR TREATING LEATHER.—*Jacques Wolf & Co., BP* 747,183. *J. Soc. Dyers and Col.* **72**, 7, 366, (1956) : A resin stable in aqueous solution is obtained by heating an aqueous solution of 3.6-5.0 mol. HCHO, 1 mol. dicyandiamide and 0.3-1.0 mol. boric acid until a product is obtained which is soluble in water on extreme dilution and which, after adding enough of a water-soluble anionic surface-active sulphonate to dissolve any precipitate first formed on adding the sulphonate, gives a precipitate with aluminium sulphate. Application of the resulting solution to leather, particularly chrome-tanned leather, which if not anionic should be rendered so by treatment with an anionic agent, results in increased weight or thickness of the leather, improved whiteness and finer and improved overall "break" (resistance to sharp creasing and attendant separation of fibres when the leather is bent).

TANNING AGENTS.—*BP.*747, 675. *J. Soc. Dyers & Col.* **72**, 7, 358, (1956). Improved stable tanning agents are obtained by adding an aliphatic aldehyde and an o-chlorophenol (having at least one free o- or p-position) simultaneously but separately into a mono- or disulphonic acid or an aromatic hydrocarbon containing at least two condensed nuclei, while condensing the resulting mixture.

BODY COLOUR OR TOP FINISH FOR LEATHER.—*Chemische Fabrik Gruinau. BP* 747, 769. *J. Soc. Dyers & Col.* **72**, 7, 366, (1956) : Incorporation of a condensate of soluble protein and/or protein decompotion products with higher fatty acids, resin acids, naphthenic acids and/or higher aliphatic or aliphatic-aromatic sulphonic acids yields products which have good adhesion to leather, glaze satisfactorily, and have good resistance to water and wet rubbing.

TANNING WITH MINERAL AGENTS AND PROTEIN CONDENSATES.—*Chemische Fabrik Grunau. BP* 748,563. *Via. J. Soc. Dyers & Col.* **72**, 9, 466, (1956) : The tanning liquor contains both a mineral tanning agent and (a) protein fatty acid condensates or (b) condensates obtained from degraded protein and high-mol. wt. carboxylic anhydrides and/or sulphonyl halides of the aliphatic or aliphatic-aromatic series or (c) ethoxy derivatives of either (a) or (b). This yields a supple leather, and if stuffing agents are incorporated in the tanning bath, stuffing of the tanned leather is unnecessary.

BATING.—*Osterrichische Stickstoffwerke. BP* 751,141. *Via. J. Soc. Dyers & Col.* **72**, 9, 465, (1956) : Use of thioglycollic acid and/or a water-soluble salt thereof instead of an enzyme results in less loss of skin substance.

TANNING.—*Boehme Fettchemie. BP* 748,563. *Via. J. Soc. Dyers & Col.* **72**, 9, 466, (1956) : Polyalkyl ether derivatives of high-molecular sulphonamides have high affinity for collagen and are readily worked into hides. They are used as tanning agents, if desired simultaneously with any other tanning agent.

PRESERVING HIDES AND SKINS FROM BACTERIAL DAMAGE.—*British Leather Manufacturers' Research Assocn. BP* 749,769. *Via. J. Soc. Dyers & Col.* **72**, 9, 465, (1956). Treatment with weakly acid, neutral, or weakly albaline aqueous solutions of stable water-soluble salts of chlorous acid, preferably alkali-metal or alkaline-earthmetal chlorites, gives good protection against bacterial attack. They can be used either alone or in brine, or can be added to the curing salt.

NOTES & NEWS

The Government of India have decided that raw sheep skins, known as "papras" weighing 700 lbs. or above per 500 skins or those measuring over 36" in length and 24" in width will be licensed freely for export from all the ports instead of being licensed, as at present, only from the Ports of Bombay, Calcutta and Rajkot.

—*HINDU*, dated 14th November 1956.

It is reported that Hawaiian Pineapple Co., has started commercial production of Bromelain, a protein digesting enzyme derived from pineapple plants. The protein-digesting enzymes are being produced for the brewing, food and leather industries. The main use in the tannery is for unhairing and dewooling.

—*Lea. Tr. Rev.* **121**, 3674, 403, (1956).

NEW ADHESIVES.—The introduction of new upper and soling materials for the footwear manufacturer, such as PVC coated cloth and the resin rubber and microcellular solings in sheet and unit forms, has provided new problems in the field of adhesive attachment. Each of these materials has its peculiar requirements in regard to the adhesive used according to the nature of the surface to which it is to be attached. Three of them, viz., EVO Stik Nos. 440, 560, and 7,400 are of a Neoprene base and the other EVOSTIK No. X103 is based on natural rubber.

—*Shoe & Lea. News*, 210, 30, (1956).

Dr. Henry Phillips has announced his intention to retire from the Directorship of the British Leather Manufacturer's Association on reaching the age of 60. He has given six months notice from August 1st. Dr. K. W. Pepper and Dr. M. P. Balfe will take over as Director and Deputy Director respectively says Leather Trades' Review.

THIS MIRACLE SUBSTANCE THAT IS CALLED LEATHER.—Y. *Nayudamma. Lea. Tr. Rev.* **121**, 3672, 331, (1956) : The author in his address to the Madras Rotary Club pointed out that leather is an ubiquitous substance and it means Rs. 50 crores to the Indian Revenue and Rs. 35 crores by way of export which could be doubled if the present tanning techniques could be modified and leather prepared in the finished form instead of exporting it in semi-tanned fashion.

PAKISTAN LOSES MILLIONS THROUGH PEST DAMAGE.—*Aminuddin Ahmed. Lea. Tr. Rev.* **121**, 3672, 332, (1956). The total losses incurred by Pakistan due to the following specific diseases and parasitic infestations of the skin, viz. mange, tick, warble fly, ringworm lice, eczema, warts and nematode, is estimated to run into millions. These diseases considerably damage the hides and skins and so a systematic survey of the occurrences of these diseases should be conducted.

AIR FORCE DEVELOPS ACID-RESISTANT LEATHER.—A two-step method for the production of experimental leathers resistant to the action of the powerful oxidants and reductants used as fuels in guided missiles has been developed by the Air Force in U.S.A., says *"American Shoemaking"*. This method, which has applications in the manufacture of shoes for wear in industrial plants, is described in a report of research just made available to industry by the Office of Technical Services, U.S. Department of *Commerce*.

The first step calls for chrome tanning, then treating by an emulsion method, through which 10 to 15 per cent of a filler polymer is deposited within the interstices of the hide. This closes most of the free spaces in the outer sub-surface leathers and also provides an anchorage for the acid-resistant film.

In the second step, a resistant polymeric film of about five to six mils thickness is deposited. From the number of polymers investigated, a few were found which give excellent acid-resistance. With this system, leathers having good physical characteristics and excellent acid-resistance were prepared.

—*Aust. Lea. J. Boot & Shoe Rec.* **59**, 2, 78, (1956).

NOTHING LIKE LEATHER ? —Someone with a flare for statistics has computed that the average step is twenty-six inches, which means 2,437 paces to the mile, or 12,185 steps waled in every five-mile day. A man of the average weight of eleven stone six pounds, therefore, will pound into his shoes over 974 tons of weight each day. By putting the life of a pair of shoes down at the very conservative estimate of three months, this statistician shows that 88,000 tons weight have been successfully combated before the shoes finally surrender. Judged on these figures, the perennial slogan that "nothing takes the place of leather" bears the impress of truth.

—*Aust. L. J. Boot & Shoe Rec.* **59**, 2, 96, (1956).

BRITAIN SENDS MORE FOOTWEAR ABROAD.—Britain last year sent 7.9 million pairs of boots and shoes to 128 countries, thus maintaining her position as the world's largest exporter of footwear.

These exports were valued at £9 million, 8 per cent. higher than in 1954, according to the annual report of the British Footwear Manufacturers' Federation.

An extra 200,000 pairs were sent to the U.S. and Canada during 1955, where earnings expanded by 850,000 dollars to 6.73 million dollars.

—*Aust. Lea. J.* **59**, 2, 34, (1956).

SOLVENT TANNAGE WILL SEE A NEW ERA IN LEATHER.—The leather industry faces a new era as a result of recent and current developments in a new phase of tanning called 'solvent tannage'. Some of the many advantages promising to come out of this development are (i) a drastic reduction in tanning time, (ii) lower labour costs, (iii) a

better quality of leather, (iv) substantially smaller amounts of tanning materials are required, (v) permits shoes to be moulded rather than lasted, thus opening up new vistas in methods of shoemaking and (vi) lowers overall costs of leather making and hence of leather.

—*Aust. Lea. J.* **59**, 3, 136, (1956).

LEATHER INDUSTRY IN SWEDEN

An important section of the Swedish Leather Industry i.e., the production of bottom leather has lost almost half of its market and it seems most unlikely that this loss will be made good.

In the spring of 1952 subventions for imported bottom hides were stopped with the result that shoe prices rose considerably, in some cases by nearly 60%. Naturally sales dropped considerably and although purchases proportionately as rubber soles have become popular.

One of Sweden's two large producers of tanning extracts has drawn the consequences of this development and have recently started a pulp factory.

The trend for uppers has been influenced by the introduction of plastic materials for the production of handbags and suit-cases. There seems to be no doubt that plastics have entered this market.

(Report received from The Joint Chief Contr. of Imp. & Exports, Madras).

TRAINING INSTITUTES FOR FOOTWEAR AND LEATHER MANUFACTURE.

The Ministry of Commerce and Consumer Industries have approved of two schemes for starting Training Institutes for footwear and Leather Manufacture at a cost of about Rs. 9 lakhs. The training Institutes would be set up in Madras and Agra. Each Institute is expected to turn out about a hundred trainees a year. The training would be both for craftsmen engaged in the industry as well as for supervisors and foremen. Sometime ago the Ministry appointed a German Expert to start a Pilot Centre in Agra. This was followed by a Footwear Centre in Madras run by the State Government. These Centres have proved very successful and a net-work of such production centres are being started ; some of these have already got under way. The Training Institutes in Madras and Agra would provide instruction and practical training in the latest method of manufacture, with the most modern type of machinery and equipment, to the workers in these production centres. In addition to the German Expert, a team of four more foreign experts in the manufacture of footwear and leather products would arrive shortly in India to act as instructors in these Institutes.

Loans and Grants totalling Rs. 55,03,427 have been sanctioned since 1954-55 to State Governments, individual cobblers, Cobblers Co-operative Societies, etc., for the development of cottage and small scale shoe and

leather industry. One Extension Service Centre for Footwear has been sanctioned, and the establishment of more such centres are under consideration. Moreover, Government have set up the National Small Industries Corporation (Private) Ltd., to help the marketing of the products.

—*J. Ind. & Trade*, **6**, 10, 1531, (1956).

SOVIET PLAN EXPANSION PROGRAMME FOR FOOTWEAR,

Russia has announced plans to increase its shoe output by 53 per cent. under its Sixth Five Year Plan (1956-60).

Directives issued by the Central Committee of the Communist party —highest governing authority in the U.S.S.R.—call for production of 455 million pairs of shoes in 1960. This compares with actual output—according to official Soviet Statistics—of 297 million pairs in 1955.

More than half of the proposed additional shoe production will come from new factories or expansion of existing ones. According to "American Shoemaking" (U.S.A., 29-2-'56) the Government newspaper "*Izvestia*" said that capital expenditure by the industry between now and the end of 1960 will provide manufacturing facilities for 85 million pairs of shoe annually.

Soviet production of shoes "of all types" increased 7 per cent. in 1955 as compared with 1954. This gain, "*Izvestia*" asserted, represented an "overfulfilment" of the government's plan for both leather and rubber shoe output during the year. The paper said that in 1955 Russian factories introduced "mechanised continuous lines" for welted shoe production.

Significantly, retail shoe sales in the U.S.S.R. increased only 3% last year as compared with the 7% output gain.

—*Aust. Lea. J.* **59**, 4, 66, (1956).

C. L. R. I NEWS

The Central Leather Research Institute participated in the UNESCO Conference Exhibition held at Delhi.

The West German Technical Mission visited the Institute on Thursday the 8th November 1956.

Dr. Y. Nayudamma, Assistant Director-in-charge, who has been appointed as Hony. Special Officer for the planning, designing and setting up The Central Arecanut Research Institute, visited Calicut to have preliminary discussions with Central Arecanut Committee.

The Chinese Agricultural Scientific Study Mission visited the Institute on 19th November 1956. A painting depicting a scenery in China was presented to the Institute by the Head of the Mission as a token of goodwill.

Mr. J. F. Farington of Messrs. Simson McConechy Co., Ltd., addressed the Leather Technologists' Association on the trade aspects of E.I. tanned hides and skins.

VISITORS

Name	*Dates of Visit.*
Dr. Gunther Becker, F.A.O. Expert from Berlin ..	7-11-1956.
Prof. Schonfeld, Prof. R. Thedick and Mr. E Duensing of the West German Technical Mission ..	8-11-1956
Mohemed A. V. Sayeh, Mr. H. A. El Samonondy and Mr. M. R. Hashim, Members of the Permanent Council of Public Services, Egypt ..	15-11-1956
Chinese Agricultural Scientific Study Mission ..	19-11-1956
Dr. and Mrs. A. F. Spilhaus, University of Minnesota, U.S.A. ..	20-11-1956
Shri Motiram Bora, Minister for Finance, Relief and Rehabilitation, Government of Assam ..	27-11-1956