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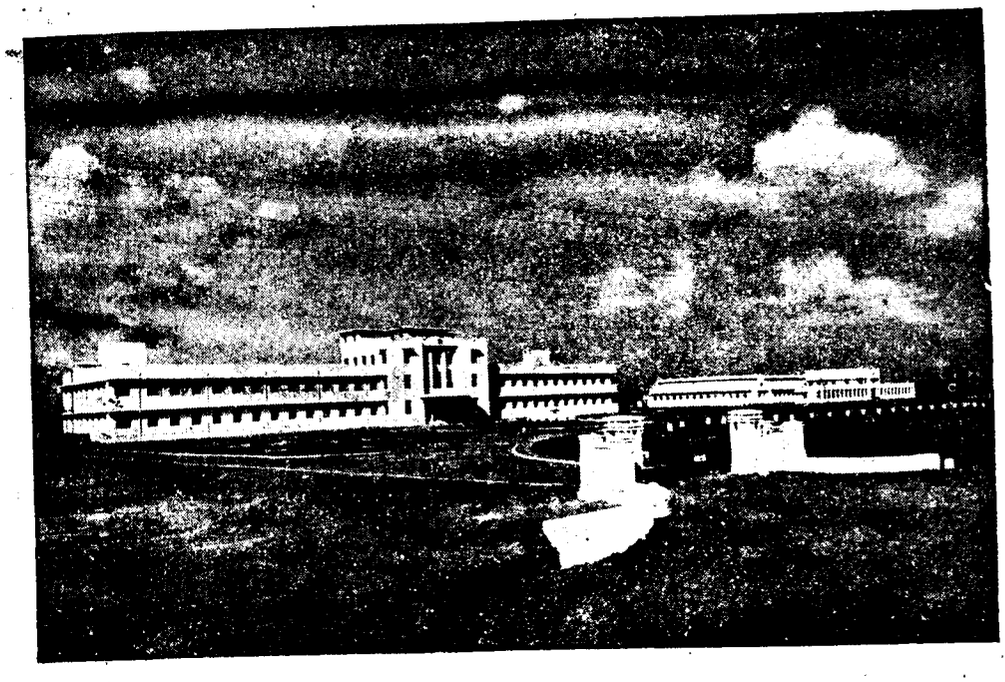

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STUDIES ON SHRINKAGE PHENOMENON: PART-IV AREA SHRINKAGE

BY

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(Received on 7th June 1958)

SUMMARY

Employing a planimeter, a method has been worked out for measurement of area shrinkage, with an error of 3%. It has been observed that the area shrinkage values thus obtained have to be interpreted with caution because the shrinkage varies from specimen to specimen, depending upon the location of the specimen in the hide or skin and also upon the pre-treatments given to it. All tannages decrease area shrinkage of pelt, to varying degrees. However, shrinkage temperature is not an indication of the resistance to area shrinkage of pelt. The ability to resist area shrinkage is enhanced when stable crosslinks are formed. In combination tannages, the combined effects of the tanning agents are reflected in the area shrinkage values. The first tannage also has an important influence. Recovery of shrunken area does not appear to be dependent on shrinkage temperature or area shrinkage or crosslinks formed or tannin fixed.

It is now well established that the shrinkage phenomenon is related to the structure and structural stablity of the skin, and the shrinkage temperature, has been generally accepted as the practical measure of the degree of 'Leathering'. A study of the shrinkage temperature and the shrinkage phenomenon has proved to be a very valuable and powerful tool for a better understanding of the inherent properties of a biological products like collagen, such as

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ples were taken from the various parts of the skin along the back-bone, butt, belly, neck and shank regions, both perpendicular to the backbone and parallel to the back-bone. The sampling positions are shown diagramatically in the sketch on page 181.

This work has been conducted on goat skin subjected to quick liming and then completely delimed and dehydrated by means of alcohol and acetone. From the data obtained in this study, it is observed that: (1) the area shrinkage values vary from region to region in the same skin, (2) area shrinkage values vary from skin to skin in the same region (3) area shrinkage values vary depending upon the treatment given to the skin. Particularly, the method of liming influences the area shrinkage to a great extent. In the case of pelt subjected to quick liming, area shrinkage increases from the back-bone to the belly regions whereas in the case of pelt subjected to long liming, no such variation was found. In the case of the goat pelts subjected to quick liming, area shrinkage values were very low in regions immediately adjoining the backbone and gradually increased to 45-50% towards the belly. The area shrinkage values in the neck and shank regions were signficantly less than those in regions like the belly. There was no clear indication of any directional effect whether the samples were taken perpendicular or parallel to the backbone.

This study clearly indicates the complexity of the problem and the need to be cautious in interpreting the results of these researches. Though the area shrinkage could be measured fairly accurately, the figures for area shrinkage for the specimen leathers collected from the various parts of the skin vary within themselves. Any further study should then be limited to selecting a chosen area of the skin whose history is well-defined. For comparative studies, however, the adjoining samples may be taken quite conveniently and the error in these cases should not be large. Further work reported in this paper is based on this understanding.

Area shrinkage of tanned leathers: Pieces of dehydrated pelt were cut from the butt area and the adjoining portions were marked for comparative tests. These pieces were tanned by the customary way with formaldehyde, basic chrome, basic aluminium sulphates, syntans, sulphonyl chloride or fish oil, used alone and in combination with formaldehyde. As it is known that formaldehyde tanned leather has a tendency to recover the shrinkage when immersed in water after shrinkage, tanning pelt with formaldehyde alone or in combination with other tannages, has been utilised for obtaining samples. It is felt that the area shrinkage measurements as well as the recovery of the area shrinkage might give a clue to the mechanism involved in these tannages. For determining the extent to which pelt and leather pieces would regain their original area, the shrunken samples were kept overnight in water at room temperature and the areas were measured after the removal of the excess water. The area shrinkage is reported as a percentage of the original area and the recovery is expressed as percentage of the area shrinkage percent. The results so obtained are reported in Table I below. The figures in the column 'under tension' refer to shrinkage obtained with load of about 45 gm applied to the leather sample in the Theis meter. For the purpose of comparison, the area shrinkage of pelt, corresponding to the region from which the sample for a particular tannage was taken, is also given.

Discussion: From the data in Table I, the following observations are made:

1. All tannages tend to reduce the area shrinkage of the pelt. However, the extent of the decrease in area shrinkage varies with the tannage. The area shrinkage is the least in the case of formaldehyde and chrome tannages and highest in the case of sulphonyl chloride tannage. This is a significant fact. It is known that in the case of chrome and formaldehyde, strong cross-links are formed during

TABLE I

Tannage	Shrinkage Temp. (°C)	Area shrinkage of		% of reduction in area shrinkage	Area shrinkage of leather under tension	Recovery of leather shrunk free
		Pelt	Leather (Free)			
1	2	3	4	5	6	7
Formaldehyde ..	87	43	16	63	7	88
Chrome ..	122	39	16	59	9	Nil
Chrome and Formaldehyde ..	118	39	11	72	10	„
Formaldehyde and Chrome ..	116	46	7	87	3	„
Wattle ..	86	42	41	2	25	„
Wattle and Formaldehyde ..	99·5	42	14	67	5	„
Formaldehyde and Wattle ..	94	35	27	22	12	„
Basic Al sulph. ..	75	37	29	22	20	„
Al sulph and F. ..	88	37	12	68	7	„
F. and Al sulph ..	85	31	27	13	11	43
Tannigan Extra A ..	66	51	32	35	21	Nil
Do. and F. ..	75	51	25	51	17	„
F. and Tannigan ..	80	32	21	34	12	37
Sulphonyl chloride ..	64	37	37	—	34	5
Do. and F. ..	83·5	19	6	69	8	127
F. and Sulph. chloride ..	83·5	45	15	66	6	66
Fish oil ..	67·5	44	18	59	14	117
Do. and F. ..	80	42	4	90	5	125
F. and Fish oil ..	68	44	11	75	7	66

Shrinkage Temperature of Pelt: 61°C.

the tannage and the structural stability is greatly improved, whereas in the case of sulphonyl chloride, no such cross-links occur and thus the structural stability is not so great.

2. In tanning with vegetable tannin, the hydrogen bonds occurring must give some degree of structural stability to the leather. The adsorbed tannin also may influence the shrinkage in area.

3. This seems to be the case with basic aluminium sulphate also where a certain amount of basic aluminium sulphate is adsorbed and where the bonds may not be as strong as in the case of chrome. The hydrolysability of the tanning compound in hot water may also tell upon the area shrinkage.

4. Fish oil, however, surprisingly shows a low degree of area shrinkage. Probably the aldehydes and peroxides formed during the fish oil tannage form firm cross-links accounting for the stability.

5. *Area recovery*: The recovery of the area is seen only in the case of fish oil and formaldehyde tannages. The recovery is more than 100% in the case of the former and about 88% in the case of the latter. The formaldehyde tanned leather is characterised by the fact the heat-shrunk leather re-extends to its original length upon cooling. This is known to be specific for formaldehyde tannage. But it appears to be the case with fish oil tannage also. In fact the recovery is much pronounced in the case of fish oil. This reaction suggests that either the cross-links do not exist in such tannages or the shrinkage does not involve the irreversible breaking of these cross-links in these leathers. Küntzel[5] applied the Meyer-Ferri concept of the mechanism of the elastic behaviour of rubber to interpret this reaction. In the melting and contraction of the fibre, the lengthwise tension is increased. The cross-sectional tension sets in upon cooling and brings about the re-orientation of the structural

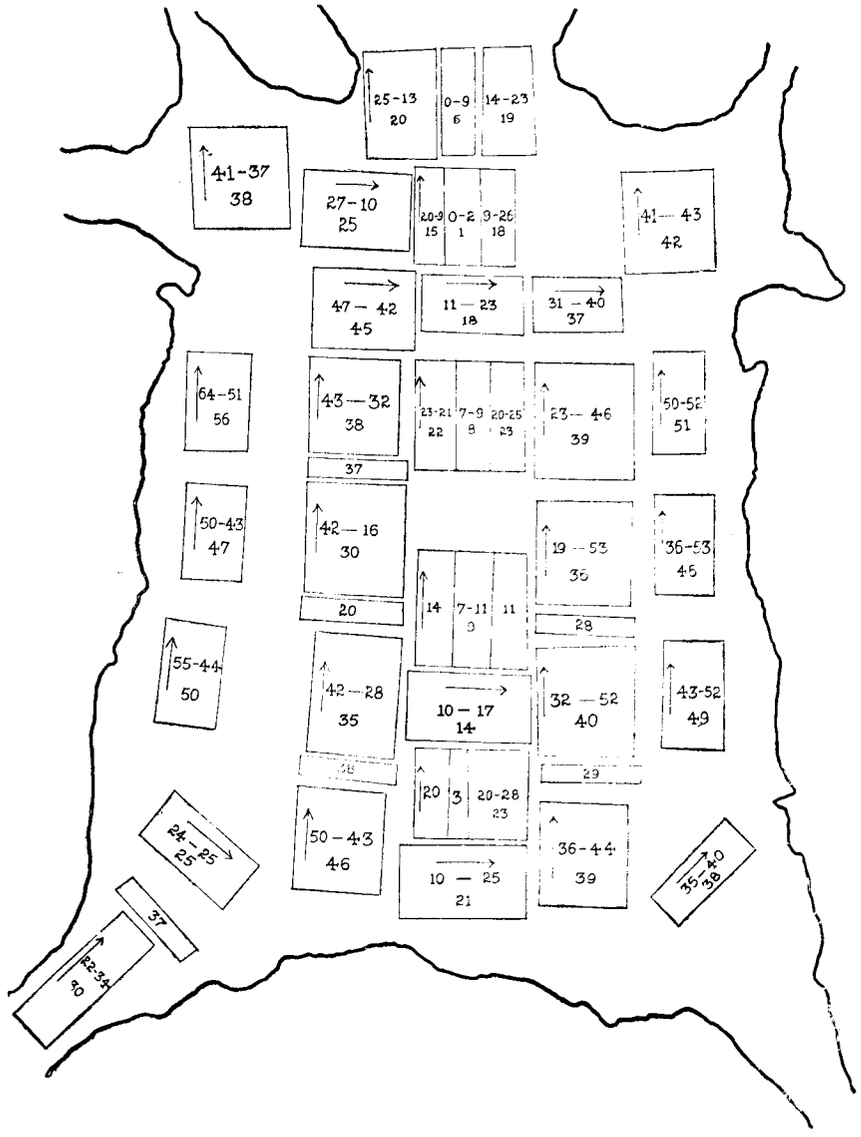
units and accordingly the elongation of the fibres. The elastic behaviour of the fish oil tanned leather and the formaldehyde tanned one would prove valuable to further interpret this observation.

6. Though sulphonyl chloride is used in place of fish oil in the tannage of chamois leather, the behaviour of the leather seems to be very different. The area shrinkage of sulphonyl chloride treated leather as compared to the pelt is negligible and the recovery of the area shrinkage is also very negligible in contrast to that of the fish oil tanned leather. It is known that in the case of sulphonyl chloride tanned leather no cross-links occur and it was expected that there would be full recovery of area shrinkage. But sulphonyl chloride treated leather behaves as if it were pelt. Evidently, the area shrinkage recovery phenomenon may or may not be related to the wettability, water absorption capacity or the amount and nature of cross-links involved. A study of this problem should prove fruitful.

The observations that may be made in regard to combination tannages with formaldehyde are as follows : —

1. *Chrome and Formaldehyde tannage* : Both chrome and formaldehyde individually enable the leather tanned with them to shrink less as compared to the pelt. This ability is further enhanced when the pelt is treated with chrome and formaldehyde. However, when the pelt is treated first with chrome and then retanned with formaldehyde, the area shrinkage is more as compared to the leather tanned first with formaldehyde and retanned with chrome. This difference is probably due to the greater amount of formaldehyde or chrome fixed in the leather tanned first with formaldehyde.

In the case of chrome leather, the recovery of area shrinkage is nil and this position is maintained whether the pelt is treated first with chrome or retanned with chrome.



The variation in the area shrinkage values over different regions of quick-limed goat pelt. The figures are percentages of area shrinkage. (The upper figures, e.g., 10-25, give the range of variation of % area shrinkage; the lower figures, e.g., 21, give the average value. The arrow indicates the direction of the length of the test piece.)

2. *Formaldehyde and Basic Aluminium sulphate combination tannages* :

The area shrinkage of leather tanned with basic aluminium sulphate is much higher than that of chrome or formaldehyde tannage indicating that the amount and the stability of the cross-links formed may not be as great as those obtained in chrome and formaldehyde tannages. The area shrinkage might also be influenced by the loosely held basic aluminium sulphate as in the case of vegetable tannage.

When pelt is treated first with basic aluminium sulphate and retanned with formaldehyde, the area shrinkage is very much reduced, probably influenced by the fixation of formaldehyde in the leather. However, the reverse is not found to be the case. The formaldehyde tanned leather has low area shrinkage but when retanned with aluminium sulphate, the area shrinkage is increased. This is probably due to the loading by the aluminium sulphate as in the case of vegetable tanning.

The recovery of shrunken area is nil in the case of leathers tanned with basic aluminium sulphate and the same retanned with formaldehyde. However, 43% recovery of the shrunken area was observed in the case of leather tanned first with formaldehyde and then retanned with aluminium sulphate, showing the influence of the preliminary tannage, namely, the formaldehyde tannage. This is not so, however, in the case of chrome or wattle tannage. Though why such recovery is observed is not clearly understood, it looks as if chrome and wattle form additional cross-links with formaldehyde tanned leather, as shown by an increase in the shrinkage temperature compared to that of leather got with formaldehyde alone, and these additional cross-links are inhibiting the ability of formaldehyde to recover. In the case of formaldehyde retanned with basic aluminium sulphate, no additional cross-links may be formed, as is shown by the shrinkage temperature being almost

the same as that of single formaldehyde tannage, and the ability of formaldehyde to recover is partly maintained.

3. *Formaldehyde and wattle combination tannage*: As compared to pelt, wattle tannage does not decrease or increase the area shrinkage. While admitting that wattle tannin may form additional cross-links with formaldehyde, there is no proof to show that Cr forms cross-links with formaldehyde. When the pelt is first treated with wattle followed by formaldehyde, the area shrinkage is much reduced. This is expected, because on retanning, formaldehyde not only forms cross-links with the protein but also cross-links with vegetable tannin forming polymerised compounds within the leather and fix permanently the adsorbed and loosely bound vegetable tannin. This might probably account for its increased resistance towards area shrinkage.

However, if the pelt is treated first with formaldehyde and then retanned with vegetable tannin the area shrinkage is considerable. Though, in the treatment with formaldehyde, the leather should have obtained stability towards shrinkage, the retanning with vegetable tannin and incorporation of a large amount of loose tannin into the leather might impart the characteristics of wattle which will not enhance the stability towards area shrinkage; the net result is that the formaldehyde leather retanned with vegetable tannin will have a lesser stability towards shrinkage. In this procedure of retannage, free formaldehyde is not available to react with the vegetable tannin and form polymeric compounds.

As in chrome-formaldehyde combination tannages, the recovery of shrunken area is nil in the wattle or wattle-formaldehyde combination tannages, bearing out the influence of wattle tannage and masking the effect of formaldehyde.

4. *Formaldehyde and Syntan combination tannages* : The syntan treatment reduces area shrinkage but not to the

same extent as formaldehyde, but the leather tanned with syntan and retanned with formaldehyde enhances its resistance to area shrinkage. When the process is reversed, i.e., formaldehyde tanned leather is retanned with syntan, the area shrinkage is further reduced and also there is a recovery of 37% of the shrunken area unlike leathers tanned with syntan followed by formaldehyde retannage, where the recovery is nil. This is similar to the case of formaldehyde tanned leathers retanned with basic aluminium sulphate.

5. *Formaldehyde and sulphonyl chloride combination tannage* : When the sulphonyl chloride tanned leather is retanned with formaldehyde, the area shrinkage is very much lowered. It is known that a great amount of formaldehyde is fixed on retanning the sulphonyl chloride treated leather and this will account for the increased resistance to area shrinkage. If formaldehyde tanned leather is retanned with sulphonyl chloride, there is also increased resistance to area shrinkage.

The difference in regard to recovered areas is of interest. When the sulphonyl chloride treated leather is retanned with formaldehyde, the recovery is 127% whereas when the formaldehyde treated leather is retanned with sulphonyl-chloride, the recovery is approximately half (67%). This is even lower than that of formaldehyde tanned leather.

Our previous studies have shown that the amount of formaldehyde fixed on retanning the sulphonyl chloride tanned leather is approximately 3 times that fixed in straight tannage and this may account for this behaviour. It would be of interest to study the area shrinkage and area recovery and their relationship to the fixed formaldehyde content.

6. *Fish oil and formaldehyde tannage* : In the case of fish oil tannage, the ability to resist area shrinkage is more as in the case of formaldehyde. This may suggest that in fish oil tannage, aldehyde tannages are involved or as in

chrome tannage, the carboxyl groups may be involved in cross-linking with the peroxides formed. But unlike chrome tannage and as in formaldehyde tannage, the fish oil tanned leather has the tendency to recover the shrunken area; when fish oil tanned leather is retanned with formaldehyde, the area shrinkage is very much reduced. This is probably due to the additive effect and reinforcement with formaldehyde linkages. Shrinkage temperature is also high; the area recovery is also increased. But when the formaldehyde tanned leather is retanned with fish oil, the area shrinkage is less as compared to the fish oil or formaldehyde tanned leathers but more than that of the fish oil tanned and formaldehyde retanned leather. The shrinkage temperature is reduced and the area recovery is also reduced. The fish oil probably breaks down some of the formaldehyde fixed in the leather as well as some of the cohesive forces of the protein itself. The pretreatment with formaldehyde makes the pelt more stable and the leather tanned first with formaldehyde followed by fish oil retannage seems to be comparatively stabler than pelt tanned with fish oil alone.

Area Shrinkage under tension. The values obtained for area shrinkage of leather under tension are generally comparatively lower than those of area shrinkage of leather in the free condition. The area shrinkage value may depend upon the load and for each different type of tannage, the load may have to vary. Also, the area shrinkage will be restricted because one dimension is fixed under the load whereas in the free state, the area shrinkage occurs in all directions. It is for this reason that the data pertaining to the area shrinkage under free conditions are compared and discussed.

Conclusions

1. It is observed that the area shrinkage values have to be interpreted with caution because the area shrinkage

varies from specimen to specimen depending upon the region of the hide and also depending upon the pretreatments given to it.

2. All tannages decrease the area shrinkage of the pelt and this implies that the tanning introduces a constraint on the ability of collagen to shrink. The shrinkage temperature is, however, not an indication in regard to the resistance to the area shrinkage of the pelt. Fish oil tanned leather with a low shrinkage temperature has the same resistance to area shrinkage as compared to the chrome tanned leather with the highest shrinkage temperature.

3. The ability to resist area shrinkage imparted by tanning varies with specific tannage. Whereas formaldehyde, chrome and fish oil tannages impart the highest resistance, sulphonyl chloride tannage gives the least.

4. This, however, brings out the fact that where stable cross-links are formed during tannage as with formaldehyde and chrome, the ability to resist area shrinkage is enhanced; whereas in the case of sulphonyl chloride tannage, where no such cross-links occur, the area shrinkage of the leather is the same as that of the pelt.

5. In combination tannages, the combined effects of the tanning agents are reflected in the area shrinkage values, probably, the amount of tanning material fixed and the number of stable links formed with individual tanning materials may also tell upon the area shrinkage phenomenon. In the case of materials such as vegetable tannins and basic aluminium sulphate where a part of the tanning material may be fixed to the leather in the adsorbed form the area shrinkage is increased. The first tannage also influences the area shrinkage factor in combination tannages.

6. Recovery of the shrunken area is known to be a characteristic of formaldehyde tannage but this is the case

with fish oil tannages also. In fact, the recovery of the shrunken area is much more pronounced in fish oil tannage than in formaldehyde tannage. However, sulphonyl chloride behaves differently from fish oil though it is used to make the same type of leather. Recovery of shrunken area does not appear to be dependent on shrinkage temperature or the area shrinkage factor or the amount of cross-links or the amount of tannin fixed in the leather. It is probably due to the nature of the cross-links that might have been formed during tannages and the elastic behaviour of the shrunken fibres in the wet-state.

7. The characteristic property of area recovery of formaldehyde tanned leather is retained after retannage with fish oil, sulphonylchloride, syntan and basic aluminium sulphate. However, this is not the case when retanning with chrome and vegetable tannin. When the leathers from chrome, wattle, aluminium sulphate and syntan tannages, are retanned with formaldehyde there is no area recovery, indicating the influence of the preliminary tannage. However, in sulphonyl chloride tannage where no cross-links are formed in the preliminary tannage, there is area recovery indicating the influence of the formaldehyde retannage.

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TECHNICAL SEMINAR

Fractionation of four Indian vegetable tannins *

E. C. MATHEW

Four Indian vegetable tanstuffs, (*Cassia auriculata, Cassia fistula, Acacia arabica* and *Hopea parviflora*), were fractionated. Fresh barks were successively and exhaustively extracted with petroleum ether, chloroform, ethyl ether, ethyl acetate, acetone, methyl alcohol and cold and hot water; the fractions were further fractionated by adsorption chromatography, silica being the adsorbent. These fractions were studied by two-dimensional paper chromatography. It was found that:

(1) the percentages extracted by different solvents for the same bark and by the same solvent for different barks were quite different,

(2) there was both similarity and dissimilarity between the different fractions of the same bark,

(3) it was not possible to isolate individual components.

* Summary of the talk given on 31-10-1958.

TECHNICAL SEMINAR

E. I. Tanning and Scientific Knowledge *

C. K. DURAIVELAN

Kalyanam & Co., Madras

E. I. tanning is not merely an art and is based on some scientific knowledge not known to the tanner himself. He should be made to realise that there is science behind the process and that scientific methods are any day better than rule-of-thumb ones.

The conventional E.I. tanner is a tanner because his forefathers were tanners. Therefore, he follows the same old conventional methods by following which he is able to produce fine leather which finds a ready market in foreign countrics. Because of an assured market and also because the product is fine, the E.I. tanner believes very little in scientific knowledge and is allergic to it. So the leather technologist and leather scientist should come down to the level of the tanner, talk to him in his own language and convince him that if he followed the efficient scientific methods newly evolved, he could be economically benefited and that under his own tannery conditions, with slight changes here and there, he could produce better quality leathers, which would fetch him a better return.

The E.I. tanner may not know that there are problems. Actually a number of problems of E.I. tanning can be posed to the leather technologist: cutting down the period of liming, use of chemicals other than sulphuric acid for deliming, prevention of wastage of tannin in tanning, blending of avaram extract with other known tanning materials, etc. Of course some of these were being tackled by the Institute. It is to be hoped that the tanner and the research worker would work in close unity to achieve substantial progress.

* Condensed from the talk given on 15-11-1958.

CLASSIFIED ABSTRACTS

PROCESSES PRIOR TO TANNING

HEATING OF PAINTED SHEEPSKINS IN PILE: Its cause and influence on the quality of basils and chrome gloving leather with relation to paint composition. *G. H. Green. J.S.L.T.C.* **42**, 304 (1958). The heating in pile of sheepskins painted with lime-sulphide paint has been shown to be due to bacterial growth on the damp, dirty wool or hair. Factors influencing heating are discussed. Soaking the skins in, or spraying the wool with dilute solutions of antiseptic prevented or delayed the onset of heating.

No damage was observed on pickled pelts or on basils tanned from lamb skins painted with paint containing 2% sodium sulphide (as Na_2S) which heated to 88-92°F, but these conditions are less severe than may attain in practice. Grain damage occurred on gloving leather under these conditions but was much less on skins painted with a sodium hydrosulphide paint of the same sulphide content which heated to 87-88°F. The results indicate that damage is related to both alkalinity of the paint and temperature reached in pile, and also to the type of leather produced from the pelt.

CHROME TANNING

THE NATURE OF THE NEUTRAL SALT EFFECT IN CHROME TANNING. EFFECT OF SODIUM CHLORIDE ON THE REACTION OF BASIC CHROMIUM SULFATES WITH COLLAGEN. *K. H. Gustavson and Magne Nestvold. J.A.L.C.A.*, **53**, 589 (1958). The effect of addition of sodium chloride to solutions of basic chromium sulfates on the composition and the hydrothermal stability of the chrome-collagen compounds (chrome leather) is as follows:

As the concentration of Cl ions increases, the collagen shows preferred affinity for them. A more or less extensive displacement of sulfate anions takes place. In solutions 4*M* in chloride, the sulfate which exists in ionic combination in the chromed collagen is displaced completely. The complexly fixed sulfate groups show greater resistance to displacement by the neutral chloride; however, about half the sulfato groups are displaceable.

A marked impairment of the hydrothermal stability of the leather is the most characteristic result. Since the decrease of the chrome fixation induced by the added salt is rather small, it is believed that this detrimental effect is caused by the changes taking place in the chromium complexes on the penetration of Cl groups, which changes impair the ability of the complexes to cross-link and stabilize the protein. A shift of the reaction in the direction of a greater number of chromium complexes combined unipointly with collagen is suggested to be the governing factor.

THE TANNING PROPERTIES OF CHROME LIQUOR PREPARED FROM ORGANIC REDUCING AGENTS. VI. The adsorption of anionic chrome complexes with organic acido radicals by hide power. *Yukichi Sakimoto, Tsugio Osugi, and Nobuyoshi Kurakata* (*Hokkaido Univ. Sapporo*). *Nippon Hikaku Gijutsu Kyokaishi* **4**, 79-85 (1958); *Chem. Abstr.* **52**, 13297 (1958). In simple Cr liquor reduced by SO_2, addition of increasing amount of alkali increased the amount of Cr precipitated; all Cr in the liquor precipitated at approximate pH 6·6. When the liquor was aged for a week after the addition of Na oxalate, Na tartrate, or Na-OAc, a part of Cr in the liquor was not precipitated by the addition of alkali. In the presence of these organic salts, the maximum amount of precipitation occurred at pH 7, and it decreased beyond this point. The maximum amount of the precipitation decreased as the content of the organic salts increased. In blended liquor, the maximum amount of Cr precipitation was proportional to the ratio of the blending, the value being in general 5-10% higher than the calculated value. Larger amount of masked Cr in the blended liquor gave larger rate of adsorption of the anionic Cr by hide powder. In prolonged tanning (5 hours), the amount of cationic Cr adsorbed was greater than that of anionic Cr. but the latter seemed to be adsorbed more rapidly than the former at the early stage of tanning.

THE EFFECT OF PRECHROMING OF HIDE POWDER WITH OXALATO CHROMIATES UPON ITS FIXATION OF VEGETABLE TANNINS. *K. H. Gustavson. J.S.L.T.C.* **42**, 312 (1958). The irreversible fixation of vegetable tanning extract constituents by collagen (hide powder), Mimosa extract being the main type investigated, is not materially altered by pretanning the hide powder with anionic chromium complexes, such as the tetra-oxalato-diol-chromiates. Pretanning of hide powder with oxalato-chromiates definitely impairs the irreversible fixation of the vege-

table tannins for brief periods of retannage with vegetable tanning extracts. However, upon prolonged retannage (2-4 weeks) a slight increase of the irreversible uptake of the vegetable extract constituents is recorded for mimosa tannins, as well as for tannic acid. Redunca wood extract (myrtan) and sulphited quebracho extract on the other hand show lowered affinity even then for collagen which has been tanned with anionic chromium compounds. On the whole, the anionic chrome tannage of collagen does not seriously interefere with its irreversible fixation of vegetable tannins.

In the initial stage of the reaction of vegetable tannins with collagen (the first few hours), the basic protein groups appear to be mainly involved. Co-ordination (Hydrogen-bonding) of the polyphenols on the keto-imide groups of the protein enters as the chief reaction in the later stage. Blocking of the basic protein groups by the anionic chromium compounds is probably responsible for the lowered tannin fixation in the early stage of retannage of the oxalato-chromiated hide powder. The small increase of tannin fixation occurring on extended periods of retannage with certain extracts is probably due to the attachment of constituents of these vegetable tanning extracts to the chromium complexes.

The findings agree with the concept that the large increase of vegetable tannin fixation which follows the pretanning of collagen with cationic chromium complexes, even on very brief periods of tanning (1-2 hours), is due to increased reactivity of the basic protein groups, resulting from inactivation of the compensating ions by the cationic chromium complexes. In the later stages of this retannage, the formation of polyphenol-chromium complexes further accentuates the increase. This is illustrated by comparative data from series of hide powder pretanned with anionic and cationic chromium complexes, showing the effect of such pretannage when vegetable retannage is performed over differing periods of time.

OTHER TANNAGES

A RAPID SOLE LEATHER TANNAGE WITH ALDEHYDES, *L. Seligsberger, C. W. Mann, and H. Clayton, J.A.L.C.A.* **53**, 627 (1958). A new method of tanning with aldehydes pointed a way towards the making of sole leather by a rapid process in which conventional vegetable extracts could be partially or fully replaced by domestic materials.

After adjusting the stock to the proper pH in the manner described previously, it is possible to reach a shrinkage temperature of 90°C. or higher in less than 24 hours by tanning with a mixture of glyoxal and formaldehyde. Afterwards, it takes only a few hours to ready the hides for immersion in rockers. Here the pretannage with aldehyde allows the use of tail liquors that are over 40° Barkometer strong and also heated to 120°F. In pilot-plant experiments, it took only 3-5 days to obtain full penetration. The largest of these experiments in which lignosulphonate alone was employed is discussed in detail. Chemical and physical data concerning the finished leather are also presented, together with some observations concerning storageability of leather produced in earlier tests.

The new rapid tannage produces a flexible but sufficiently firm type of sole leather such as is in demand to-day, without a sacrifice of colour or heat resistance.

CHROME-IRON TANNING COMPOUND. *Eduardo Silvino Rodriguez. Rev. fac. cienc. quim., Univ. nacl. La Plata* **29**, 5-11 (1955-6); *Chem. Abstr.* 52, 14206 (1958). Ferric salts may partially replace Cr. in tanning. $FeSO_4$ may be used with $Na_2Cr_2O_7$ in tanning compounds as oxidation occurs. Recommended conditions for tanning with these materials are as follows: total Fe+Cr as oxides, 4-4·5% of the bated weight; ratio of Cr_2O_3 to Fe_2O_3 1 : 3. The original pH of the bath should be less than 2·5 for penetration. Hydrolysis of Fe salts is avoided by complexing with phosphates and organic polyhydroxy acids. The tannage should end at pH 4 to fix the metals to the collagen fiber; this basification is conducted as in normal Cr tanning. This tannage affords a 60% saving in Cr salts over normal Cr tanning.

IRON TANNAGE. VIII. THE SORPTION AND BRIDGING REACTION. EFFECT OF THE STERIC FACTOR. *Minoru Kuzota (Tokyo Inst. Fisheries) Nippon Hikaku Gijutsu Kyokaishi* **4**, 86-92 (1958); *Chem. Abstr.* **52**, 12296 (1958). The particle weight of colloid cation was measured for sols of ferric salts by a diffusion method. The particle weight increased with basicity at a definite molar concentration, and with concentration at a definite basicity. In basic $FeCl_3$ solution, the sorption attained a maximum at 2·5 *M* and 40% basicity while the particle weight rose to approx. 2000 (mol. wt. equiv.). The bridging action of Fe tannage in the presence of various dicarboxylic acids (C_4-C_{10}) was established from the shrink temperature. The acids having

C_5-C_7 showed most favourable effect. With adipic acid, the brid-ing reaction reached a maximum at one quivalent of acid to one sorbed Fe atom in the Fe-tanned leather; this maximum was attained at pH 4. Aromatic dibasic acids showed a similar saturation and are advantageous in controlling bridging reaction. There was no significant difference in the effect between fumaric and maleic acids and between phthalic and terephthalic acids. Ethylenediaminetetraacetic acid was found to decrease the shrinking temperature of the Fe-tanned leather, for it acted as detanning agent.

PROCESSES AFTER TANNING

WATER ENDS PIGMENT FINISH SAHARA. *H. L. Keinle, Leather & Shoes,* **136**, No. 7, 18 (1958). Most of the finishing problems are created through ruthless removal of water. Very high temperatures should be avoided in the drying tunnel. The application of the finish should supplement the fatliquor by providing more lubrication and moisture and combining with the fibres, so that the gel like structure of the finish rounds up the fibres and gives the leather more substance. When the leather is too dry, the moisture in the finish is absorbed and the finish is unbalanced and when dried too quickly, will give a crusty film easily breaking up. Using more finish and less water is a mistake.

Modern finishes dry much faster and have good adhesion, so much so less number of coats are applied. However, enough water must be present to aid penetration, spreading and level covering of their cells, by thorough filling of the fibre. Deficiencies in the finish may be due to need for special compounding and also low priced materials, used instead of acrylic resin. Use of nitrocellulose lacquer back coat without a protective base coat under the lacquer also leads to drying out of the leather. Typical recipes are given for tight full grain waist belt stock, wallet leather, side leather, splits and sheep skins.

—*V. S. P.*

TESTING

MARKING OF PROTEINS WITH FLUORESCENT DYE. *H. Uehleke (Deutsche Forschungsaustalt für Psycriatne, Max Planck Inst., Munich). Naturwissenschaften* **45**, 87 (1958); *Chem. Abstr.* **52**, 12045 (1958). Fluoresceinsulfonyl chloride (*I*) reacts almost quantitatively with free NH_2 groups to give very stable sulfonamides which are visible under ultraviolet light. Fluoresceinsulfonic acid, prepared from sulfophthalic acid and resorcinol, was allowed to react with PCl_5 to give *I*. *I* was added to the

buffered protein solution, stirred for 2-3 hours, and the excess dye removed by dialysis to give the marked protein. The binding of the dye to the protein was shown by electrophoretic separation of a mixture of marked animal protein and β- or γ- globulin, which had been kept overnight at 37°, to be of satisfactory stability. Only the band of marked protein was visible under ultraviolet light; photoprints were prepared easily. The method can be used for the quantitative estimation of antibodies (marked) in the presence of antigens. Fluorescent derivatives of naphthalene, xanthine, and acridine can be employed.

CHROMATOGRAPHY OF ORGANIC ACIDS. *M. Naguib and E. Beerbom (Bakteriol. Inst. Milch., Kiel, Ger.) Kiet. Milchwirtsch. Forschungsber.* **9**, 161-75 (1957); *Chem. Abstr.* **52**, 12045 (1958). A technique is described based on desirable features of those currently in use. Silica gel (2·2 g.) is mixed with 1·1 ml. 0·4 *N* H_2SO_4 until a fine powder is obtained which passes through a 0·06 mm. sieve. $CHCl_3$ saturated with 0·05 *N* H_2SO_4 is added to the powder to yield a uniform suspension. The 260 × 8 mm. column is washed with $CHCl_3$, the silica-gel suspension is introduced, and the supernatant $CHCl_3$ is allowed to drain under 0·1 atmosphere pressure. Benzene saturated with 0·05*N* H_2SO_4 is passed through under pressure until a thin layer remains above the column. The material is added to the column in the form of a silica-gel adsorbate (approx. 0·02 ml. containing 100 micromoles total acid). The sample layer is covered with a thin layer of glass wool. Fifty ml. benzene saturated with 0·05 *N* H_2SO_4 is placed in one funnel and anhydrous ether in another. By means of a mixing vessel, the ether concentration of the eluent is progressively increased. Fractions (0·7 ml.) are collected every 2 minutes by means of an automatic fraction collector. One hundred and forty fractions followed by forty 4·2 ml. fractions are collected in a 9-hour period and titrated with 0·001*N* NaOH. The maxima in terms of their respective acids are identified on the basis of preliminary experiments in which known acids are added to the column and in which paper chromatography is employed. In order in which they are eluted from the column the acids are: butyric, propionic, acetic, fumaric, pyruvic, succinic, lactic, ketoglutaric, malic, and citric. Succinic, lactinc, and trans-aconitic acids are resolvable. Examples are given in which rumen contents are analyzed for butyric, propionic, and acetic acids, and a *Pseudomonas aerogenes* culture for butyric, propionic, acetic, formic, pyruvic, malic, α-ketoglutaric, lactic, and citric acid.

TWO-DIMENSIONAL PAPER CHROMETOGRAPHY OF HIGHER FATTY ACIDS. *C. Michalec (Karlov Univ. Prague). Biochim. et Biophys. Acta* 28, 212-13 (1958) (in English); *Chem. Abstr.* **52,** 12049 (1958). In the 1st run, ascending chromatography is carried out with 93% AcOH as mobile phase, developing 5 hours at 20°. The chromatogram is dried at 80-90°. The 2nd chromatography is run 16-20 hours at -8° with 85% HCO_2H/AcOH/-H_2O (50/50/5, by vol.) as solvent. The separated compounds are identified with $Cu(OAc)_2$ and $K_4Fe(CN)_6$ or with $Hg(OAc)_2$ and dipenylcarbazone. Application of the method to the isolation of the higher fatty acids of blood serum is described.

COLORIMETRY OF FAT PRODUCTS. I. FATTY ACIDS. W. Weigel (II. Med. Univ. Klin. Charite, Berlin). *Pharmazie* **11,** 786-91 (1956); *Chem. Abstr.* **52,** 14197 (1958). W. discusses the colorimetric method of determination of fatty acids he is publishing elsewhere. The colorimetric fatty-acid number indicates content of both free and combined acids and is, therefore, comparable with the saponification number; it is based on the extinction of 0·5 mg. fatty acid in a mixture of 6 ml. concentrated H_2SO_4 and 0·5 ml. 10% aqueous HCHO (HCHO reaction) read in a layer 0·5 cm. thick with filter S43 (Pulfrich photometer). The HCHO reaction provides a quantitative fatty-acid determination and also a fairly precise characterization of small amounts of fatty acids; thus the necessity is avoided for conducting preliminary identification studies (as of splitting fats and isolating fatty acids). The method is of particular value for serial comparative determinations on small amounts of substances.

A LABORATORY SCREENING TEST OF BACTERICIDES FOR USE IN SHEEP-PELT SOAKING PITS. *J. H. Richardson (Armour & Co., Chicago). Appl. Microbiol,* **6,** 142-5 (1958); *Chem. Abstr.* **52,** 12437 (1958). A laboratory test has been designed to evaluate bactericides for use in sheep-pelt soaking pits. The following bactericides reduced the bacterial count by more than 95% (at the concentration indicated): Iobac, 0·40%; Iosan, 0·40%; PhHgOAc, 0·05%; Na_2SiF_6, 0·25%; $(NH_4)_2SiF_6$, 0·10%; $ZnSiF_6$, 0·05%; $MgSiF_6$, 0·15%; Cu 8-quinolinolate, 1·0%; *o*-benzyl-*p*-chlorophenol *o*-phenylphenol (Socci 6137), 0·5%; 2-benzyl-4-chlorophenol (Socci 6125), 0·5%; pyridinethione Na salt, 0·0001%; 3-cocotetrahydropyrimidine, 0·5%; 3-soyatetrahydropyrimidine, 0·5%; 2-methyl-3-cocotetrahydropyrimidine, 0·5%; 2-methyl-3-soyatetrahydropyrimidine, 1·0%; 2-methyl-3-tallowtetrahydropyrimidine, 1·0% gelatin thiocarbamate pentachlorophenolate, 0·5%; Armac C, 0·5%; Duomac C, 0·25%; Duomac T, 0·5%; Duomeen T, 0·5%; Duomac C and Ethofat 242/25, 0·2%.

X-RAY STUDY OF α-β TRANSFORMATION IN KERATIN. *V. D. Gupta (Univ. Allahabad). Indian J. Phys.* **32,** 42-4 (1958); *Chem. Abstr.* **52,** 12943 (1958). The degree of order Ω, introduced in the α-β transformation in keratin fibers is defined as $\Omega = [I_e - I_m)/(I_e + I_m)] \times 100$, where I_e and I_m are the intensities of the equatorial and meridional reflections, resp., in an x-ray photography. Ω was determined for black, white, and golden hair in the supercontracted, unstretched, and stretched conditions, and when treated with cupra-ammonium hydroxide in which case $\Omega = 0$. The behaviour of golden hair is nearer that of black than of white.

A NEW COLORIMETRIC PROCEDURE FOR THE DETERMINATION OF LYSINE. *J. C. Sanahuja and D. Seoane (Univ. of Buenos Aires, Arfg.) Anales bromatol. (Madrid)* **10,** 165-73 (1958); *Chem. Abstr.* **52,** 13839 (1958). Lysine (*I*) reacts with diazotized *p*-nitroaniline (*II*) in alkaline alcohol solution to form a red solution with an absorption maximum at 520 mμ. The determination is carried out as follows: Add 1 ml. of *I* solution to a 15 ml. graduated tube, dilute to 5 ml. with H_2O and 1 ml. of freshly prepared *II* (dissolve 1·5 g. *p*-$NO_2C_6H_4$-NH_2 in 40 ml. concentrated HCl, add 40 ml. H_2O and when dissolved dilute to 500 ml. with H_2O; to 25 ml. of this solution add 0·75 ml. 10% aqueous $NaNO_2$). After 5 minutes add 3 ml. of 16% aqueous Na_2CO_3. After 20 minutes dilute to 15 ml. with a solution containing 40 g. NaOH, 100 ml. 95% etOH and 140 ml. H_2O, mix and read colour, using as a reference a solution containing H_2O in place of *I*. Twenty to 300γ of *I* can be determined. Arginine and histidine interfere with the determination. An ion-exchange separation procedure will be described later.

MICROANALYSIS OF AMINO ACIDS. I. A NEW MODIFIED NINHYDRIN REAGENT. *Takeo Tsukamoto, Tetsuya Komori, and Nadao Kinoshita (Univ. Kyushu, Fukuoka). Pharm. Bull. (Tokyo)* **5,** 363-6 (1957); *Chem. Abstr.* **52,** 13829 (1958). The photometric determination of the ninhydrin-produced colours of amino acids separated by paper chromatography depends for its accuracy on the production of the highest possible colour and on the stability of the coloured end product, Ruhemann purple. The method of

Yamagishi *et al.* was, therefore, modified chiefly by the addition of HPO_3 to stabilize the ascorbic acid used in the ninhydrin reagent. To 50 cc. 2% methyl Cellosolve solution of ninhydrin was added 50 cc. 2% HPO_3 solution containing 0·075 g. ascorbic acid, and the obtained 1% nin-hydrin reagent was stable for 2 days. To 1 cc. standard solution of amino acid was added 1 cc. of the ninhydrin reagent, the mixture kept at pH 5 by citrate buffer, heated 20 minutes at 100° on a H_2O bath, and the optical density of the resulting deep purple colour determined within one hour at 570 mμ. This modified method is less sensitive to NH_3.

AN X-RAY STUDY OF SOME LEATHERS. *D. M. Chakraburtty and B. Chakravarti (Indian Assoc. Cultivation of Sci., Javadpur, Calcutta). Indian J. Phys.* **32**, 10-12 (1958); *Chem. Abstr.* **52**, 14206 (1958). The spacings of the diffuse intense band of some leather samples were studied from x-ray difraction photographs. The variation of spacing (4·32-4.74 A.) is explained on the basis of the collagen-gelatin model of Pauling and Corey which predicts a spacing of 4·72 A.

RELATION BETWEEN THE PHYSICAL PROPERTIES AND THE CHEMICAL COMPOSITION OF VEGETABLE-TANNED SOLE LEATHER. *Rinjiro Sasaki, Yasushi Sato, and Yutaka Tamai (Tokyo Univ.). Nippon Hikaku Gijutsu Kyokaishi* **4**, 74-8 (1958); *Chem. Abstr.* **52**, 13298 (1958). The specific gravity and shrinking temperature of samples taken from various parts of vegetable-tanned sole leather had no significant relation with the chemical composition of the leather, but the sample with the largest specific gravity contained the largest amount of water soluble matter and the one with the smallest specific gravity contained the smallest amount of soluble matter. The tensile strength of hide fiber/unit sectional area increased with the amount of tannin combined to the fiber. When the sum of combined tannin content and the soluble matter in the leather increased, the percentage of elongation of the leather decreased. Higher contents of combined tannin and fat were correlated with greater abrasive resistance. Larger amount of CaO decreased the abrasive resistance. The contents of the total ash, insoluble ash, and soluble ash had no relation with any of the physical properties of the leather examined.

AN INTRODUCTORY PSYCHOPHYSICAL STUDY OF BREAK IN LEATHER. *Milton Bailey. J.A.L.C.A.* **53**, 568 (1958). One of the most important characteristics of leather which concerns tanners and large consumers of leather is the property called break. Break is the system of wrinkles formed when the vamp of a shoe, is flexed during walking. Since the number of the wrinkles is related to durability, appearance, and over-all grade of leather used in footwear, it is essential that this quality be carefully evaluated. The need for an objective for evaluating break is especially emphasized by the failure of traditional visual, subjective inspection procedures to define or curb the use of coarse-breaking leathers in footwear. To solve this problem, an investigation of the break characteristic was undertaken. This work resulted in the development of an instrument called a Leather Grainometer. The instrument helped to define break objectively. Utilizing the Leather Grainometer, inexperienced personnel appear able to grade breaks more accurately and consistently than experienced commercial and technical personnel using the subjective, visual approach.

THEORIES

N-TERMINAL AMINO ACIDS OF BOVINE EYE LENS PROTEINS. *H. Bloemendal and G. ten Cate (Univ. Amsterdam). Nature* **181**, 340-1 (1958); *Chem. Abstr.* **52**, 12942 (1958) - N-terminal amino acids of the main lens proteins, α-, β- and γ- crystallin were determined. The terminal amino acids found in α-crystallin (expressed as moles dinitrophenyl amino acid per 100,000 g. dinitrophenyl protein) were glutamic acid 1·00, serine 0·12, glycine 0·07, alamine 0·05, and threonine 0·02. The very small quantities of serine, glycine, alamine, and threonine may represent either impurities still present in the preparations or terminal groups resulting from partial breakdown of the peptide chain. Preliminary experiments on β- and γ -crystallin showed the same N-Terminal amino acids (mainly glutamic acid) to be present, although in different proportions. This might be an expression of (serological) organ specificity of these proteins.

TANNINS. EFFECT OF TANNIN AND ITS RELATED COMPOUNDS ON LYSINE AND ARGININE DECARBOXYLATION BY ACETONE-DRIED POWDER OF ESCHERICHIA COLI. *Koichi Kimura, Shigeaki Kuwano, Hiroshi Hikino, and Yasuko Sasaki (Univ. Osaka). Yakugaku Zasshi* **78**, 296-8 (1958); *Chem. Abstr.* **52**, 12072 (1958), Tannin and allied substances inhibited the decarboxylation of lysine and arginine by Me_2CO-dried cells of *E. coli*. The inhibition by gallotannin was far more marked in Me_2CO-dried than intact cells and this seemed to confirm

the fact that the apparent weak inhibition was due to the difficulty of penetrating the cell membrane. Other substances had the same tendency to inhibit with Me_2CO-dried as with intact cells. This inhibition was not overcome by pyridoxal.

TANNINS. V. EFFECT OF TANNIN AND ITS RELATED COMPOUNDS ON THE DECARBOXYLATION OF BASIC AMINO ACIDS BY ESCHERICHIA COLI. *Koichi Kimura, Shigeaki Kuwano, and Hiroshi Hikino (Univ. Osaka) Yakugaku Zasshi* **78**, 236-41 (1948); *Chem. Abstr.* **52**, 12072 (1958). Tannin (*I*) and allied substances inhibited the decarboxylation of basic amino acids by *E. coli*. The inhibition by *I* is comparatively weak and this is probably due to the permeability of cell membrane. Phenol-carboxylic acids (*II*) have stronger inhibitory action than poly-phenols lacking CO_2H group and the activity of *II* is decreased by esterification. Thus, the presence or absence of a CO_2H group has a great effect on the degree of inhibition. This inhibition is not antagonistic to coenzymes, is not overcome by cysteine, and is not competitive with the substrate.

VARIATION OF ASPERGILLUS ORYZAE. XVI. THE VARIATION INDUCED BY CHEMICALS. 10. *Kei Yamagata. Hakko Kogaku Zasshi* **35**, 394-7 (1957); *Chem. Abstr.* **52**, 13861 (1958). Previously it was reported that *A. oryzae* successively cultivated in a medium containing Zn-EDTA (ethylenediaminetetraacetate) was inhibited in its nicotinic acid-synthesizing ability by addition of 1 mg. cystine/ml. medium and that the inhibition was removed by addition of guanine, hypoxanthine, or xanthine. Similar studies were extended with Cu, Fe, Mg, and Mn media. The *A. oryzae* cultivated successively in Cu-EDTA or Mn-EDTA medium was not inhibited by cystine; addition of guanine or xanthine showed no effect. In the media containing Fe-EDTA or Mg-EDTA, the nicotinic acid-synthesizing ability of *A. oryzae* was markedly inhibited by cystine and the inhibition was removed by guanine and xanthine. The *A. oryzae* cultivated for 5 generations in a medium containing Zn, Fe, Cu, or Mg salt was inhibited more by cystine than this mold grown in a medium containing corresponding metal-EDTA. Maximum inhibition of nicotinic acid-synthesizing action by cystine was 95% in Zn salt medium, 90 in Fe medium 85 in Cu medium, and 70 in Mg medium. When these *A. oryzae* strains were transplanted to media containing corresponding metal-EDTA complex, the inhibition by cystine was observed to a lesser extent; with Cu medium, the removal was 95%, Fe 50%, and Zn 40%. The results indicate that the variation induced by cystine is unstable and that the metal-EDTA complex has specific activity. Of the S-containing amino acids examined, cystine was found to be most active in inducing variation in *A. oryzae* cultivated in media containing one of the above salts. Cysteine followed and methionine and taurine had considerably smaller activities. Other amino acids, e.g., proline, serine, leucine lysine, alanine, and trytophan showed the activities comparable to the last 2 S-containing acids. Cystine and cysteine produced no complex with Cu and methionine and taurine did it only to a slight extent. The inhibition of the nicotinic acid-synthesizing ability of *A. oryzae* was significantly observed with cysteine, methionine, and taurine as with cystine, but not with proline, leucine, and lysine, showing that the inhibition is related to the S in the former group of amino acids.

THE FLAVONE PIGMENTS OF THE POLLEN OF ACACIA DEALBATA. *V. Alberto Spada and Riccardo Cameroni (Univ. Modena, Italy). Gazz. chim. ital.* **86**, 965-79 (1956); *Chem. Abstr.* **52**, 12092 (1958). The evaporated eluate containing the flavone glycosides is placed on a 2nd column of powdered cellulose and the chromatogram developed with BuOH saturated with H_2O. One fraction, evaporated *in vacuo*, taken up in MeOH, let stand several days at 0°, and recrystallised from aqueous MeOH yields yellow needles, m. 269°. This substance yields 1 mol. glucose and 1 mol. myricetin on hydrolysis, and its behaviour with $ZrOCl_2$ indicates that the 3-position is blocked; it is therefore *myricetin 3-glucoside*. A 2nd fraction, after repeated paper chromatography in BuOH-AcOH-H_2O (4: 1: 5), yields rutin. Another portion of the H_2SO_4 solution is freed of alcohol by distillation, brought to a concentration of 3% H_2SO_4, and hydrolyzed by boiling. The aglycones are identified by their chromatographic behaviour and colour reactions; quercetin and myricetin are found, and the presence of robinetin and morin is confirmed. Ultraviolet absorption curves are given. *VI. Ibid.* 980-9. The filtrate from the Pb $(OAc)_2$ precipitation is precipitated with basic Pb acetate, the precipitate is washed and suspended in H_2O, the solution is brought to pH 2 with H_2SO_4, filtered, deacidified with Amberlite, concentrated, and left in a desiccator for several months. The crystalline mass is fractionally crystallised from Me OH-H_2O, yielding prunin and a 2nd substance (white needles, m. 154-5°). The latter substance furnishes 1 mol. naringenin and 2 mols. glucose on hydrolysis; methylation with CH_2N_2 followed by hydrolysis gives naringenin 4′, 7-dimethyl ether; hence the substance is *naringenin 5-diglucoside*.

PATENTS

MODIFIED ALKYD RESINS. *Rohm & Haas G.m.b.H. (Ernst Seifert, Inventor)*. **Ger. 915,745**, July 29, 1954; *Chem. Abstr.* **52**, 12459 (1958). Alkyd resins are modified with dihydroxydicyclopentadienyl vinyl ether (*I*) before, during, or after formation of the alkyd resin at relatively low temperature so that premature cross-linking is avoided. Thus, 11g. of a 1·25% BF_3-Et_2O solution was added to 180 g. *I* and 180 g. linseed oil. The mixture was heated to 100° for two hours. Then 38 g. glycerol and 3 g. Ca linoleate were added and the mixture stirred for one hour at 270° to interchange the ester radicals. After cooling to 100°, 45·5° g. phthalic anhydride was added. After stirring for 5·5 hours at 270°, formation of the alkyd resin was complete.

SYNTHETIC WATER-SOLUBLE TANNING AGENTS. *Farbenfabriken Bayer, A.G. (Heinz Schultheis, inventor)*. **Ger. 939839**, *Mar.* 1, 1956; *Chem. Abstr.* **52**, 13299 (1958). Carbazole is sulfonated with H_2SO_4 to obtain a carbazoledisulfonic acid (*I*), if necessary with addition of compounds containing sulfonic acid and (or) OH groups, such as naphthalene-, or naphtholsulfonic acid, in the presence of water and aromatic mono- and (or) polyhydroxy compounds or other substance, such as PhOH, cresol, urea, thiourea, or guanidine, which are capable of reacting with, e.g., croton-aldehyde or hydroxybutanedisulfonic acid (*II*). *I* is condensed with lower saturated aliphatic aldehydes, such as HCHO, at 80-120°. The resulting solution is neutralized with inorganic or organic bases. Lower aliphatic carboxylic acids are then added until a pH of 2-5 is reached. For example, 170 g. carbazole was added to 195 g. H_2SO_4.- H_2O at 100°, giving a medium-brown paste which was stirred at 100-5° for one hour, cooled at 85-90°, and 50 cc. water added. Then 250 g. of a tech. phenol mixture was added. The mass was heated at 95° and, during the next 90 min. 400 g. 50% *II* and 140 g. 30% HCHO were dropped in through a reflux condenser. The solution was heated at 100-5° with stirring until SO_2 formation stopped and the solution was clear. After 1 hour it was cooled at 80° and neutralized with 25% aq. NH_3. The neutral sirup was acidified to pH 2·5-3 with 50 g. glacial AcOH and 20 g.HCO_2H. The resulting tanning agent (*III*) was readily soluble in water and useful as dispersion medium for vegetable tanning liquor. By use of *III* alone, bright and flexible leather was obtained.

DEGREASING OF HIDES AND FURS. *Badische Anilin-& Soda-Fabrik Akt.-Ges.* (Siegfried Grunler and Werner Kunzer,

inventors). **Ger. 913,094**, *June* 8, 1954; *Chem. Abstr.* **52**, 13300 (1958). Hides and furs are degreased by treatment with aqueous emulsions of chlorinated hydrocarbons prepared by aid of saponified products of sulfochlorination products of high-molecule saturated hydrocarbons as emulsifiers. Preferably, the products obtained by treatment of the sulfochlorination products of high-mol. saturated hydrocarbons with low-mol. aldehydes and NH_3 are used as emulsifiers. Emulsion concentrates are first made by addition of small amount of water to the emulsifiers. These are then diluted with additional water for use in degreasing.

TANNING AGENTS. *Farbenfabriken Bayer A.-G. (Heinz Schultheis and Detlev Delfs, inventors)*. **Ger. 941,681**, *Apr.* 19, 1956; *Chem. Astr.* **52**, 14207 (1958). Solid water-soluble nontanning aromatic polycarboxylic acids which do not form insolule Ca salts, in free or partially neutralized form, are used as components of solid or powdered tanning agents in mixtures with solid vegetable or synthetic tanning agents, optionally along with additional acid-reacting substances. Preferably, polycarboxylic acids are used which are intermediate or final products of the total oxidation of petrified or charred plant material.

FINISHING OF SPLIT LEATHER, LEATHER WASTE, AND SIMILAR PRODUCTS. *Isar-Chemie G.m.b.H. (Friedrich Zimmer, inventor)*. **Ger. 863540**, *Jan.* 19, 1953; *Chem. Abstr.* **52**, 14207 (1958). A layer of an elastic-plastic, self-hardening polymer is applied to the surface of the material to be finished followed by the spreading of another layer to serve as the carrier for embossing. Thus, split leather, on the knife side, was wetted and brushed with 10 parts of a vinyl chloride-vinyl acetate copolymer in 90 parts MeCl. After drying, another coat, containing 1-2 parts dioctyl phthalate, was applied, followed, after drying, by a final spray of pyroxyline- containing plasticizer and (or) pigment, and embossing.

LEATHER GREASING AGENTS. *Zchimmer & Schwarz vorm. Chemnitz (Rudolf Schwarz, Hans Wulf, and Maximilian Hussong, inventors)*. **Ger 944,630** *Nov.* 29, 1956; *Chem. Abstr.* **52**, 14208 (1958). Tanned, neutralised and (or) dyed leather is greased successively with two or more different greasing agents. The one which gives deep greasing consists of animal, vegetable, or synthetic oils, and may also contain partially or completely sulfonated or sulfated mineral oils, or oils which have been made water-soluble or dispersible in water by acid resistant emulsifiers, e.g., ethylene oxide condensation products. The other greasing

agent imparts surface greasing. It also consists of the same oils and fats, which have been made water-soluble or dispersible by means of fatty acid salts.

FIXATIVES FOR TANNING MATERIALS. *Deutsche Goldunsilber- Scheideanstalt vorm. Roessler (Franz Köhler, inventor).* **Ger. 865,309**, *Feb.* 2, 1953; *Chem. Abstr.* **52**, 14207 (1958). The condensation products of 'diacylates' of α,β-unsaturated aldehydes with N-containing compounds having the general formula NRR′R″, in which R, R′, and R″ are H, alkyl, hydroxyalkyl, cycloalkyl, aryl, aryalkyl, or heterocyclic groups, are suitable fixing agents for all types of tanning materials in both acid and alkaline media. Thus, 'acrolein diacetate' (*I*) 39·5 was mixed with 15% NH_4OH 68 and, after the exothermic reaction was complete, boiled for 1-2 hours with glacial AcOH 30 parts. The product was a red-brown, clear, water-soluble liquid. *I* 39·5 and $HOCH_2CH_2NH_2$ 15·25 parts were boiled for 2 hours to give a viscous, clear, red-orange product. *I* 31·6 and $(HOCH_2CH_2)_3N$ 29·8, boiled with glacial AcOH 12 parts for 15-20 minutes yielded a clear, viscous, orange product. *I* 26·5 and 15% Me_2NH (added in 2 increments) 90 parts, boiled for one hour yielded a clear, water-soluble red-brown product which was particularly effective in fixing tanning materials from a dilute solution. *I* 79 and 15% NH_4OH 140 boiled for 1-2 hours with 80 parts $EtCO_2H$, give a product which, after adjusting the pH to 7·0 functioned satisfactorily with all types of tanning materials.

CHROME SULFITE CELLULOSE AND ALUMINIUM CHROME SULFITE CELLULOSE SOLUTIONS FOR TANNING LEATHER. *Z. A. Rudnitskii.* **U.S.S.R. 110,956**, *June* 25, 1958; *Chem. Abstr.* **52**, 14207 (1958). The oxidation-reduction reaction between purified sulfite cellulose extract and chromate is carried out at a nearly neutral pH, e.g. 5-6. To obtain an AlCr sulfite cellulose solution, Al salts, e.g., $Al_2(SO4)_3$ or Al alums, are added to the chrome sulfite cellulose preparation.

TREATMENT OF HIDES. *Rohm & Haas G.m.b.H. (Otto Grimm, inventor).* **Ger. 944,454**, *June* 14, 1956; *Chem. Abstr.* **52**, 14207 (1958). The degree of swelling of soaked and washed animal hides in the alkaline tanner's pit is diminished by first treating the hides with a solution of neutral salts, e.g., $MgCl_2$, $CaCl_2$, NaCl, KCl, NH_4Cl, $ZnCl_2$, $MgSO_4$, Na_2SO_4, HCOONa, or $AcONH_4$.

DYEING OF VELOUR LEATHER. *Sandoz A.-G. (einzz Wicki, inventor).* **Swiss 325,058**, *Dec.* 14, 1957; *Chem. Abstr.* **52**, 14208 (1958). Velour leather is dyed to even and deep shades by tumbling in a rotating dye vessel with a cold solution containing a wetting agent and concentrated acid or substantive dye, followed by further tumbling in a hot dye liquor containing smaller amounts of additional dye. Thus, Cr-tanned sheepskins were treated with a mixture of bis (hydroxyethyl) dodecylaminotriglycol ether, after-tanned with a mixture of K and Cr alum, and dried. About 100 parts of the leather were then placed in the vessel, agitation started, and a cold solution containing 6 parts Chloramine Black BH (Colour Index No. 401) and 120 parts water was added. After tumbling for 45 minutes an additional 700 parts water (70°) was added and the mass was tumbled for 30 minutes. The bath was then exhausted by adding 2 parts 85% HCOOH and, after 20 minutes more tumbling, the liquor was drained off. A fresh liquor containing 8 parts dye and 800 parts water (70°) was then added, tumbled for 30 minutes, and exhausted as above. The dyed leather was then diazotized in the usual manner with methylphenylene-diamine, developed, dried, and finished. An even and deep-black dyed leather results.

ALKALINE DECOMPOSITION OF LEATHER WASTE. *Elektrochemische Fabrik Kempen-Rhein Dr. Brandenburg & Weyland G.m.b.H. (Fritz Hess, inventor).* **Ger. 867,048**, *Feb.* 16, 1953; *Chem. Abstr.* **52**, 14208 (1958). Leather waste is boiled under mildly alkaline conditions, as usual in glue manufacture to decompose it to an extent of 60-80%, followed by boiling under stronger alkylation to yield low-molecular protein derivatives. Thus, 1000 Kg. Cr-leather waste, conaining 33% dry matter, was boiled with a solution of 30 kg. magnesite in 6 cu.m.water. After filtration, the resulting 4600 l. of liquid was a 5% glue solution. The residue was heated 2 hours at 120° in an autoclave with 30 kg. 50% NaOH, resulting in 600 l. of a liquid containing 6 kg. protein-decomposed products and a residue consisting mainly of Cr hydroxide.

COMPOSITIONS FOR IMPARTING WATER RESISTANCE TO LEATHER. *Alfred W. Hopton.* **U.S. 2,827,432**, *Mar.* 18, 1958; *Chem. Abstr.* **52**, 12440 (1958). Leather stuffing compositions including at least one member of the group consisting of fat, oil, wax, and petrolatum and containing an activating ingredient in an amount of 4-75% by weight are used to give water vapour-permeable, water-impermeable leathers. The activating ingredient is either a sterol or a water-insoluble hydrocarbon monosulfonate whose molecular weight is at least 470. These sulfonates have the general formula $R(SO_3M)_n$, in which R is a hydrocarbon

radical containing > 27 C atoms, M is a univalent metal or NH_4, and n is 1 or more. The ratio of n to the number of C atoms in R should not exceed 1: 27. Petroleum sulfonates may be used. The sterol is conveniently obtained by de-esterification of wool fat. Organic sulfates, such as sulfated oils, will not serve as activators.

WATER-RESISTANT LEATHERS. *Ian C. Somerville and Richard F. M. Fisher (to Rohm & Haas Co.)* **U.S. 2,824,816**, *Feb.* 25, 1958; *Chem. Abstr.* **52**, 12440 (1958). A solution of a hydrophobic impregnant in a hydrophobic solvent is drummed with leather until equilibrium is reached. A hydrophilic solvent which is miscible with the hydrophobic solvent and which is a poor solvent for the impregnant is added to deposit the impregnant on the leather fibres. The impregnated leather is drained and dried. When the impregnant is of the thermosetting character, heating during drying is controlled to produce the desired polymerization or condensation of the impregnant within the leather. In an example, 20 lb. of a copolymer obtained by polymerization of 1 part hexadecyl methacrylate and 2 parts octadecyl methacrylate was dissolved in 400 lb. of an aliphatic hydrocarbon mixture (b. 300-90°F). The resulting solution was used to treat 100 lb. of glove-leather-type, chrome tanned horse fronts (treated with 10% fat liquor, dried and staked) by drumming for 3 hours. Exhaustion of co-polymer onto the leather fibres was accomplished by addition at 3·05 hour intervals of 10% by volume of a solution of 90% iso-PrOH. After a final drumming period of 0·5 hour, the skins were removed, drained, and hung in a warm room (110-20°F) to dry for 48 hours. The resultant skins had a soft, mellow feel, retained their original colour, had no solvent odor or tacky feel, and withstood 5000 flexes in the Maeser water-resistance test before the first leakage of water occurred. The total water absorbed and transferred through the leather at this point was only 1 g. The impregnants include polymers of at least one monoethylenically unsaturated compound; polymers of at least one ester of acrylic, methacrylic, or itaconic acid with higher aliphatic alcohols containing 8-30 C atoms; and long-chain isocyanates and ketenes containing 8-30 C atoms. The hydrophobic impregnant may also be a water-insoluble polymer of a compound having the formula CH_2: CRCOOANHCONH$_2$, in which R is Me or H and A is alkylene group having 2-14 C atoms. The hydrophilic solvent contains at least 3 parts H_2O, methoxyethnol and iso-PrOH being cited. Tallow, octadecyl isocyanate, and octadecyl ketene are specifically cited impregnants.

BYE-PRODUCTS

CHEMICALS FROM WOOD, *Chester Placek, Bruce J. Buhmann, and Richard T. Galganski (Marathon Am. Can Co., Rothschild, Wis). Ind. Eng. Chem.* **50**, 570-6 (1958); *Chem. Abstr.* **52**, 13254 (1958). A method of recovering useful materials from spent sulfite liquor (*I*) is described. *I* is treated with lime in 3 stages to precipitate $CaSO_3$ (*II*) and Ca lignosulfonate (*III*). The filtrate from the 3rd stage, which contains salts of organic acids, is treated with Na_2CO_3 to form the Na salts and is filtered, evaporated and sold as a 50% solution or dried. *II* is returned to the acid plant. *II* can be acidified and treated with Na, Mg, or Al salts to form solutions of metallic lignosulfonates. *III* can be converted into vanillin, the effluent (*IV*) from which is evaporated to 50% solids and temperature is demethylated and desulfonated in Dowtherm units. This yields a boiler water-treating compound. *IV* can be acidified to precipitate lignin which is treated with NaOH to form Na lignosulfonate. Products of the operation include *oil-well cement retarders, tannins, boiler-water-treating compounds,* and *III* having 20% reducing sugars which is hygroscopic and is a dispersant.

GENERAL

HAZARDS IN TANNING AND SOME REMEDIES. *Carl & Conklin. Leather & Shoes,* **136**, No. 6,14 (1958). Hazards associated with wringing and setting are chrome poisoning, back strains, slips and falls. The first is prevented through use of protective equipment. Back strains can be prevented by maximum use of mechanical equipment. Prevention of falls can further be helped by slip-resistant footwear. Back strains and falls are also caused in sorting blues. By proper guarding, hazards in splitting and shaving can be minimised. Slips, falls and strains are associated with colouring and setting out operations, during which floors are slippery. Good instruction, good house-keeping and safety footwear prevent these. These play an equally important part in conditioning also. While a majority of hazards in buffing are removed through use of improved guarding, completely suitable guards are not yet devised for staking machines. Proper type of venting equipment would prevent formation of explosive vapours during finishing. By proper guarding of the presses, it might be made impossible for the operator to be caught in the machinery.

— *V. S. P.*

NOTES & NEWS

GRIM POSITION OF THE BRITISH UPPER LEATHER INDUSTRY

In the full chrome upper leather section of the leather industry, imports have risen from less than 10% of U.K. Production to 50% mainly owing to low priced imports from Commonwealth countries. Over 80% of these imports come from the Commonwealth countries of Australia, India, Ireland and Canada in order. The U.K. production has declined by 11% from the 1949 level. Since 1949, the industry has been prevented by the rising flood of imports, from reaching its planned production levels. The bulk of the imports is of low to medium quality leather in the standard black and brown colours. Thus the low priced imports are concentrated into a narrow quality range, which depresses the price the U.K. tanner can obtain for his own equivalent production. The price at which much of the imported Commonwealth leather is sold is below fair market price — owing to the gross ineffectiveness of the Anti-Dumping Act of 1957.

India, by a ban on raw hide exports, a prohibitive import duty of 75%, on finished leather, combined with a licensing system which would bar any leather that surmounted the tariff wall, gives her tanners a buyer's market in raw materials and a completely protected market in finished leather. The Irish Republic doubled her import duty in 1951. It is difficult to escape the conclusion that the Government is simply frightened of doing or saying anything which would offend commonwealth countries and further, that it is frightened perhaps of retaliation. However, the U.K. remains the largest single open market in the world. Therefore, the Commonwealth countries concerned would be unwilling to offend their biggest customer.

The present policy of maintaining the U.K. as a wider open duty-free market completely removes all incentive on the part of the Commonwealth leather exporter to look for any other market.

While a complete abolition of imports from Commonwealth countries, would not be pressed for, voluntarily agreed quantitative arrangements are called for.

— *Leather Trades' Review* — 20-8-1958.

LEATHER INDUSTRY IN SOUTH AFRICA

During the past year the South African tanning industry maintained its 1956 level of production and processed just under one million hides, 90% of which were wet-salted and the bulk of the remainder dry-salted. S. A. tanners consume the majority of available wet-salted hides, whilst the poorer quality dry-salted and wet-salted hides are mainly exported.

Total sales of bottom stock were down by 7·3% on 1956 figure of 16,891,000 lbs. Upper leather production was up by 4·6%. Exports of upper leather were less than 1% of production. South Africa is, however, not self-sufficient in upper leather and altogether £3,476,000 worth of lining, upper and speciality leathers were imported for the footwear industry.

Nearly 21 million pairs of footwear were made in 1957.

— *Leather Trades' Review*, **129**, 283 (1958).

PAKISTAN'S BRIGHT FUTURE IN THE INDUSTRY

Pakistan's leather industry, if properly organised, can provide the country with an additional foreign exchange of Rs. 100 million annually.

This is stated in a survey of the Leather Industry of Pakistan, prepared for the National Planning Board by Kenneth E. Bell, a Leather Engineer of an American firm of consultants.

The report says : The Pakistan Leather Industry, if it improves the quality of its products, can compete in the world market, and can provide employment for an addition 67,000 people. Pakistan possesses abundant raw materials — many unique — and labour capable of fine handiwork, but it is essential to organise them so that their potential is utilised fully.

— *Leather Trades' Review* — 10-9-1958.

EXCLUSIVE REPORT ON AIR FORCE LEATHER RESEARCH

THERMALLY STABLE GLOVE LEATHER. In a programme of developing flight gloves, not shrinking when exposed to flash fires, it has been found that boron salts impregnated into leather result in increased resistance to shrinkage. Such boron salts were deposited from a water solution and therefore, were not permanent. Organic complexes and compounds of boron when used, gave excellent resistance to flame and also to leaching. Leathers treated showed negligible shrinkage when exposed to the flame of a Bunsen burner for 12 seconds.

ROCKET FUEL RESISTANT GLOVE LEATHER. Treatment of leather with polymer emulsions and then coating the surface with flourinated polymers, results in a leather resisting the action of red fuming nitric acid and other oxidising agents used in rocket propulsion.

OIL RESISTANT GLOVE LEATHER. Polymers containing polar groups have been found to be more effective than those not containing them, in lowering oil absorption by leather. However, oil would penetrate through the seams of gloves made with such leather and thus destroy their insulating value. So by proper modification of tanning and of suitable polymer, leather absorbing less oil and from which the oil can be extracted with gasoline without damage to the properties of leather, has been developed.

FUNGICIDES FOR LEATHER. 2,2′ dihydroxy, 5,5′ difluorobiphenyl and 2,2′ dihydroxy, 5,5′ difluorobiphenyl sulfide are promising fungicides.

FUNGICIDAL TANNAGE. Fungicides, on account of their toxicity have to be used in very small quantities. Further they are additives and so can be leached out. So work has been initiated on developing a tannage containing fungicide as an integral part of the molecule failing which developing a fungicide substantive to leather.

It has been established that chrome tanned leather is actually detanned by action of perspiration.

— *Leather & Shoes.* **135**, No. 25,12 (1958).

EMBOSSED LEATHER APRONS

Embossed leather barbecue aprons were introduced recently by American Meat Institute of Chicago. Split cow hides, calfskin, pig skin or sheep skin barbecue aprons can be mass produced to retail at $7·50 up. Professional fire fighters have long known the basic virtues of leather barbecue aprons. Fireman's helmets are made from leather because leather is heat resistant and scorch-proof. Leather barbecue aprons have the same value. Moreover they will last a lifetime and become more beautiful with use.

Four other leather product ideas introduced by the AMI staff, are leather calling cards, leather convention badges, leather plaques and leather awards and ribbons.

Leather & Shoes. **135**, No. 26,14 (1958).

'HUMANE' SLAUGHTER

Under the new American legislation slaughter shall be carried out by humane methods only. 'Humane' methods include those where 'animals are rendered insensible to pain by a single blow, or gunshot or an electrical, chemical or other means that is rapid and effective, before being shackled, hoisted, thrown, cast or cut'. Slaughtering in accord with 'ritual' requirements of the Jewish faith also is humane.

— *Leather & Shoes.* **13**. No. 6,18 (1958).

NAVY TESTS PROVE LEATHER HAS 50% GREATER WEARABILITY. Actual tests by Naval personnel have proved that leather properly impregnated wih elastomer compositions has 50% greater wearability than non-impregnated leathers and at least 35% less water absorption. This is the finding of the National Bureau of Standards.

Laboratory tests conducted by the National Bureau of Standards indicate that water absorption and abrasive resistance are directly proportional to the amount of impregnant deposited on the amount of the leathers' thickness; only elastomers with a molecular weight of less than 10,000 can effectively penetrate the leather. Best results are obtained with impregnants incorporating elastomers such as polybutene, poly-isobutylene or butyl rubber in combination with resins. To eliminate the affecting of dimensional stability, the elastomers are blended with a semi-hard hydrocarbon resin or with a polymerised rosin in a 2:3 proportion. A low viscosity solution was made by mixing together equal parts of the blended substance and a petroleum solvent.

— *Leather & Shoes.* **136**, No. 12,16 (1958).

ASSOCIATION OF LEATHER TECHNOLOGISTS, UNIVERSITY OF MADRAS

A meeting of the Association of Leather Technologists of the University of Madras, was held at the Central Leather Research Institute, on Saturday, the 15th November, 1958. Shri C. K. Duraivelan, M.A., B.L., of Messrs. Kalyanam & Co., Madras, spoke on E.I. Tanning and Scientific Knowledge. A summary of his talk is given on page 183. Dr. E. C. Mathew, Senior Scientific Officer, Central Leather Research Institute, presided on the occasion.

C. L. R. I. NEWS

The Practical Demonstration of the process on the manufacture of Picking Bands by Sulphur Oil Vegetable Combination Tannage as part of Extension Service Programme has been started at the College of Leather Technology, Calcutta, on the 16th November, 1958.

The Practical Demonstrations at Jullundur have been successfully completed. Much interest has been evinced by the Trade in these demonstrations.

Mr. A. Aten, Rural Industries Specialist of the F.A.O., visited the Institute on the 12th November, 1958, and discussed problems with regard to the techniques employed in the preparation and processing of hides and skins.

Shri P. M. Mathai, Director (Industries), Ministry of Community Development, visited the Institute on the 12th November, 1958, and discussed problems with regard to extension service programme for conducting practical demonstration of the processes worked out by the Institute, at Community Development centres, under the All India Khadi & Village Industries Commission.

Dr. Y. Nayudamma, Director, visited Bombay and Rajkot in connection with the organisation of Extension Service work.

Dr. Nayudamma, Director, and Dr. S. K. Barat, Assistant Director, attended he Indian Standards Convention held at Delhi between 24th and 29th November, 1958.

Dr. E. C. Mathew, Junior Scientific Officer, has been appointed as Senior Scientific Officer, Grade-II.

Dr. T. S. Ranganathan, Senior Scientific Assistant, has been appointed on promotion as Junior Scientific Officer.

Shri R. Bhaskaran, Senior Scientific Assistant has been appointed on promotion as Junior Scientific Officer.

Shri J. C. Deb, Senior Scientific Assistant, has been appointed on promotion as Junior Scientific Officer.

Dr. W. Madhavakrishna, Junior Scientific Assistant, has been appointed on promotion as Junior Scientific Officer.

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