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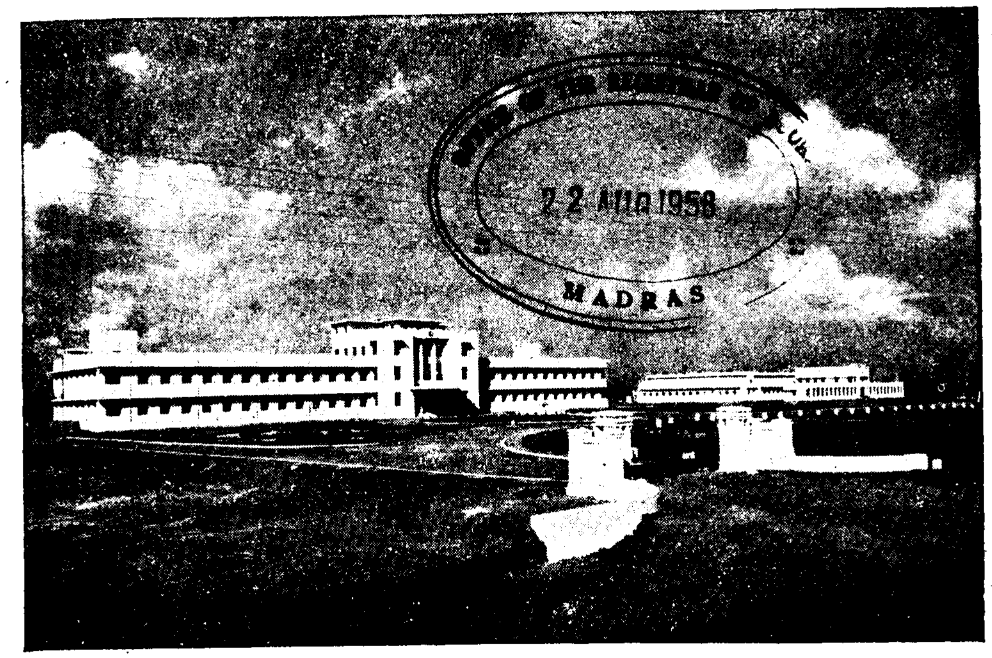

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THE INTER-RELATIONSHIPS OF THE PHYSICAL CHARACTERISTICS OF CHROME RETAN UPPER LEATHERS *

BY

N. RAMANATHAN AND D. V. SUBBALAKSHMI

Central Leather Research Institute

SUMMARY

The inter-relationships between the various physical characteristics of chrome retan upper leathers have been examined by the use of correlation coefficients. For the first time, elongation and stiffness factor have been correlated with the other physical properties. Tear strengths show a fair correlation among themselves. Elongation at break has a positive tendency to associate with the tear strengths. The inclusion of a few chrome leathers improves the correlations between the various physical properties of the leathers investigated probably because the first tannage decides to a large extent the physical characteristics of the retan leathers.

Introduction

The inter-relation between the physical characteristics of leather is one of the leading problems of leather research. The difficulty in arriving at a solution to this problem lies not only in the complex entities called hides and skins but also in their complicated combination with tannins, knowledge of which is as yet very incomplete. Perhaps the fascination is all the more because of the enormity of the work remaining to be done in the field. As happens very often in technology, utilitarian aspects press upon us the necessity for evolving standards for commerce far preceding a fundamental investigation on the basis of cause and effect.

*Part of this work was presented at the Indian Standards Convention, 1958, at Madras.

It is for the purpose of evolving Indian standard specifications that a series of physical tests were undertaken on chrome retan upper leathers. The physical tests usually prescribed for this purpose are tearing strength test and grain crack test. However, the opportunity was utilised to test the leathers for some more properties such as tensile strength and stiffness with a view to determine any inter-relationship that might exist between the various physical characteristics. The materials tested included a few chrome uppers for purposes of comparison. The retannages were not restricted to a particular vegetable tannin as various retannages are met with in industry.

Experimental

Both light and heavy leathers were used for the investigation. The essentials of the treatments involved in the preparation of the various leathers are as follows.

In the case of light leathers all the hides were first tanned with chrome in the usual way and then with one of five different vegetable tannages (10% extract), viz., Cutch, Quebracho, Myrab, Wattle and Gambier. Heavy leathers were first tanned with chrome and then given the following treatments: (a) Cutch retannage and fat-liquored with soap, (b) Cutch retannage and fat-liquored with sulphonated Pongam oil and free Pongam oil, (c) Cutch retannage and hand stuffed, (d) Quebracho retannage and hand stuffed, (e) Cutch retannage and double bath fat-liquored, (f) Fat-liquored, (g) Hand stuffed.

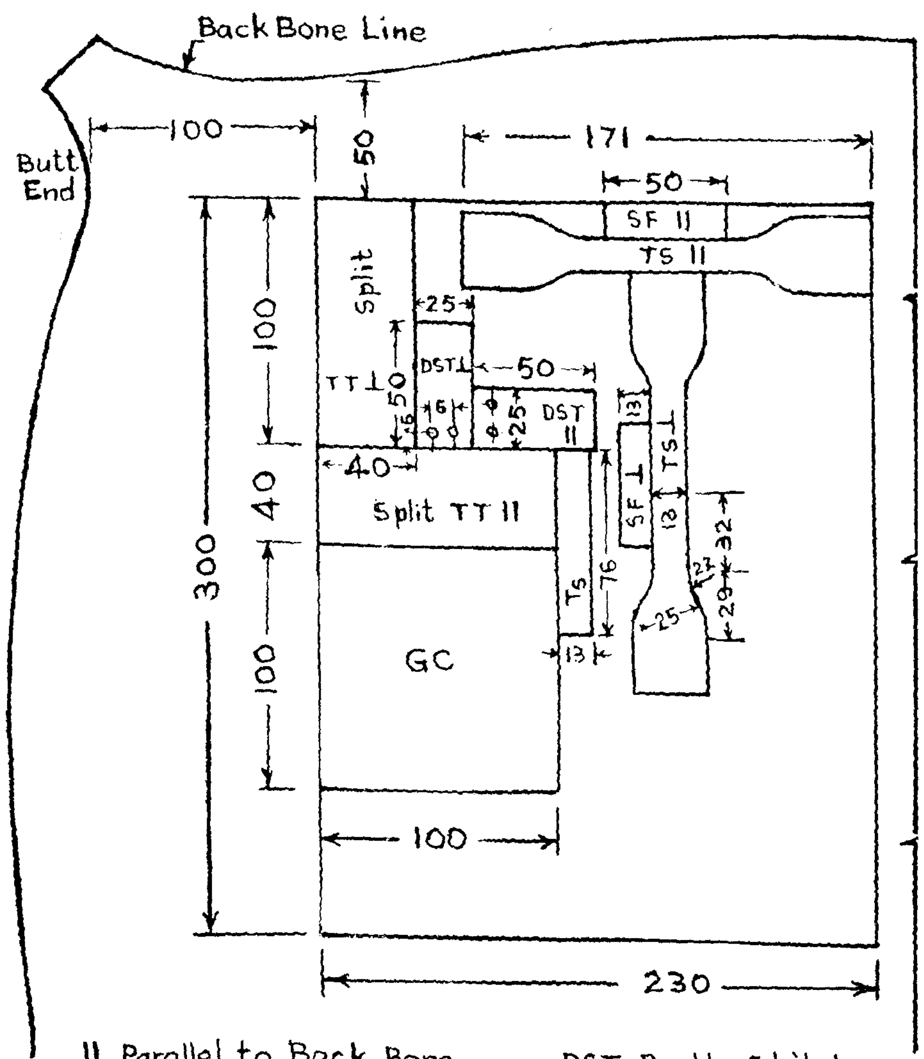
The procedure adopted for obtaining the test samples was to get first a piece 30 cm. × 23 cm. in the location shown in the accompanying sketch and then cut out the individual marked portions. The samples were conditioned in an atmosphere maintained at 80° ± 4° F temperature and 65% ± 2% relative humidity for more than a week. A Scott tensile strength tester- type J- with the rate of traverse of the lower jaw at 10 inches per minute, was used for the

tensile strength, elongation, tongue tear strength and double hole stitch tear strength tests. The stiffness factor was determined with the help of a Tinius Oslen Stiffness Tester-6 inch-pound capacity—operated by an electric motor.

Details of the dimensions of the test specimens are given in the sketch. The tongue tear specimens were split in the middle starting from one end and over half the length as shown. The two free ends were clamped in the two jaws of the testing machine. For testing the double hole stitch tear strength, two holes of diameter 5/64″ (2 mm.) were punched out at a distance of ¼″ (6 mm.) from one end and ¼″ (6 mm.) from each other as illustrated. A soft metal wire 0·04″ in diameter was bent into a U-shape and the two limbs were passed through the two holes such that the free ends of the wire were on the flesh side. The wire ends were clamped in the upper jaw and the free end of the leather specimen was clamped in the lower jaw. The sample for the stiffness test was placed grain side up with one end clamped in the vice and the other resting on the loading pin. In this arrangement, the grain side would become concave on bending as happens when a shoe is used. In the tongue tear test, care was exercised in clamping the specimen so that the direction of split was parallel to the axis of the tester which is the direction of application of the tensile force. Otherwise the tear would take place in other directions and the load readings would be different. Similar care was taken in the double hole stitch tear test to see that the U-shape of the wire was maintained and the limbs of the wire were parallel to the direction of pull.

Results and Discussion

As leather is an unhomogeneous fibrous material, its physical properties vary over a fairly wide range. The statistical analysis of the results obtained is therefore indispensable. For the purpose of assessing the extent of an inter-relationship, the correlation coefficient has been



ll Parallel to Back Bone
⊥ Perpendicular to Back Bone,
TS Tensile Strength.
TT Tongue Tear
DST Double Stitch
SF Stiffness Factor
GC Grain Crack
Ts Shrinkage Temp.

PROCEDURE FOR OBTAINING TEST SAMPLES OF LEATHER
(All dimensions in millimetres)

TABLE I

t-test (95% confidence level)

	Tensile strength (lb./sq. inch)	Elongation at Break %	Double hole stitch tear (min.) (lb./inch)	Double stitch tear (max.) (lb./inch)	Tongue tear (min.) (lb./inch)	Stiffness factor (lb./sq. inch)
(a) *Chrome retan light leather*						
Lower limit ..	2738	30·3	644	887	87	716
Mean ..	3006	32·5	724	985	102	843
Upper limit ..	3274	34·7	804	1083	117	970
(b) *Chrome and Chrome retan heavy leather*						
Lower limit ..	2851	34·4	639	788	89	547
Mean ..	3212	38·0	740	891	107	671
Upper limit ..	3573	41·6	841	994	125	795

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employed. If the correlation coefficient is +1 or −1, the correlation is perfect, the former indicating that the two properties considered increase in value simultaneously, and the latter that one of the properties increases in value while the other decreases proportionately. A zero value indicates complete absence of correlation and intermediate values denote varying degrees of correlation. Another useful statistical test is the t-test, which is used when the number of observations is small. This enables us to determine a range within which the mean of a large number of observations or the population mean is expected to lie at a certain confidence level and also to know if two sets of observations can be considered to belong to the same population. In testing different types of tannages like chrome-vegetable and chrome alone or leathers of different weight ranges such as those designated 'light' and 'heavy', the t-test was applied to the small number of observations associated with each type in order to determine the feasibility of combining the different tannages or the different weight ranges for purposes of correlation. The results are given in Table I. It is seen that the light and heavy leathers could be treated as one lot for the purpose of correlation. However it was thought desirable to combine the light chrome retan and heavy chrome retan leathers on the one hand and the heavy chrome retan and the heavy chrome leathers on the other, as this would give us an opportunity for assessing the effect of including chrome leathers in the analysis.

The correlation coefficients for the various pairs of physical properties are given in Table II. In this table (Min) and (Max) indicate respectively, the load required to start the tear and the maximum load recorded in the course of the tear. It is the minimum load-(min)- that is required for specifications but the maximum load is also recorded for the sake of interest. The stiffness factor (S.F.) was obtained by use of the formula $(4S/wd^3) \times (M \times \text{Scale reading}/100A) = \text{S.F.}$, where 'S' is the span in inches i.e., the distance be-

TABLE II

Correlation Co-efficients for the Tests Taken in hours

	1	2	3	4	5	6	7	8
1. Tensile Strength ..		+0·253	+0·041	−0·113	−0·098	—	+0·168	+0·607
2. Elongation at break (%) ..	+0·244		+0·265	+0·143	+0·365	—	−0·058	+0·389
3. Double Hole Stitch Tear Strength (Min.)	+0·154	+0·263		+0·668	+0·545	—	+0·066	+0·253
4. Double Hole Stitch Tear Strength (Max.)	+0·783	+0·415	+0·703		+0·553	—	−0·002	+0·311
5. Tongue Tear Strength (Min) ..	+0·475	+0·537	+0·622	+0·704		—	+0·233	+0·286
6. Tongue Tear Strength (Max.) ..	+0·124	+0·729	+0·611	+0·653	+0·742		—	—
7. Stiffness Factor ..	+0·217	−0·323	+0·023	−0·069	−0·113	−0·345		—
8. Grain Crack ..	—	—	—	—	—	—	—	

tween the grip of the vice and the loading pin, which was ½″ in this case, 'w' is the width of the specimen in inches, 'd' is the thickness in inches, 'M' is the maximum bending moment indicated on the weight attached to the pendulum and of value 0·15 inch-pounds in this investigation, 'A' is the angle in radians through which the specimen is bent and the 'Scale reading' is the corresponding reading on the load scale attached to the tester and which gives percentages of M.

In Table II, the coefficients top of the diagonal line are obtained by combining light and heavy chrome retan leathers and those in the bottom half refer to the combination of all heavy leathers. On the whole, the correlation coefficients are higher in the latter case showing that the inclusion of chrome leathers has resulted in a better correlation. Stiffness factor and elongation at break do not fall into the category of strength tests. They are two more of the important mechanical properties of leather, and, elongation and bending do take place when the leather is used. In fact, in bending, elongation and contraction are inherent. It is no doubt true that the elongation considered here is that resulting from the application of a tensile stress and may not be of the same nature as that resulting from a flexure. Further, a contraction is simultaneously taking place in bending and the overall change in the dimensions of the leather must doubtless be complex. It is perhaps for this reason that the stiffness factor correlates poorly with elongation. The coefficients between stiffness factor and the other properties were calculated, though with poor results, because of the fact that flexural and tensile forces act on the leather through the medium of the structure of the leather, which after all decides the various physical properties.

Tensile strength and elongation are closely associated properties, and in the case of single fibres, a high tensile

strength is usually associated with a low elongation at break and vice versa. In the case of the leathers under investigation, a small positive correlation has been found. This arises no doubt due to their complicated weave patterns. The correlation between elongation and other strength properties, viz., double hole stitch tear and tongue tear show a positive trend. Tensile stress is applied in all the cases and a certain amount of elongation takes place in the tear tests though not to the same extent as in the tensile strength test. The trend can thus be explained. The mechanism of the break in the tensile strength and tear tests are however different and a further detailed investigation is necessary before a conclusion is reached in this respect. The tear tests themselves correlate better. This is due to the mechanism of the tear being similar; in double hole stitch tear the wire breaks through the structure and in the tongue tear test the structure gives way due to the two-way pull on the unsplit portion. The start of the tear in both the cases is in a direction parallel to that of the application of the tensile force. It may be mentioned in passing that in the tongue tear test the tear takes place right through a length of 5 cm. resulting in a variation in the indicated load. As a matter of interest, the maximum load reached was also recorded, this being indicated as (Max) in the tables. An attempt was made to correlate the mean of the load required to start the tear and the maximum load with the other properties. This gave us poor results and it is to be concluded that the mean is not related so much as the minimum load with the other characteristics. In the case of the double hole stitch tear test, the length traversed before the complete rupture is very small but the difference in the loads required for starting the tear and the maximum is in general large and hence both the loads were recorded. The correlation between the maximum and the minimum loads in both the types of tear tests is fairly good. Tensile strength correlates to a marked degree with grain crack and to this extent, tensile strength test appears to be a useful test for upper leathers.

Conclusions

The samples used in this investigation represent a variety of chrome retanned leathers and a few chrome leathers. It was not our purpose to correlate the physical properties of leather of a particular tannage as such work has been done,[1, 2, 3] though not including elongation at break, stiffness factor and the maximum and minimum values of tear strengths. Keeping in view the variations in the treatments, the extent of the correlations obtained is no doubt worthy of note. It also appears possible to consider that the inclusion of a few chrome leathers improves the correlations, a probable reason being the fact that the first tannage is common to all and the value of the properties of the retanned leathers is mostly influenced by the first tannage.

Acknowledgements

The authors have great pleasure in recording here their sincere thanks to the Control Laboratory and the Tannery Division of the Central Leather Research Institute for their help in supplying the leather samples and the Director for granting permission to publish this paper.

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RESEARCH BEARS FRUIT

Practical Demonstration No. 2

(Second Series)

Manufacture of Semi-alum Upholstery Leather*

BY

R. SELVARANGAN, M.A. GHANI, Y. NAYUDAMMA & (late) B. M. DAS

Introduction

Upholstery leather is used not only in cars and furniture, but of late, in making box, travellers' bags and folio cases also. This type of leather has to be soft, pliable, strong, non-stretchy and of fast colour. The finished surface should not become brittle or cracked on aging. Also the leather should not deteriorate in strength and appearance on exposure to air and light and after use for a reasonably long time. In Europe and America, upholstery leather is made by chrome or chrome vegetable or vegetable tannage of the grain and middle layers split from thick spready cow hides. Such hides are not available in India. Medium and small sized cow hides, are available in lightly vegetable tanned condition. In order to get full and supple upholstery leather from these, it is necessary to retan them. Vegetable and chrome retannage do not give satisfactory leather and experiments carried out at the Institute, have shown that upholstery leather of quite satisfactory quality could be obtained by retanning vegetable tanned hides with basic aluminium salts. A process for manufacturing two-tone

* Process demonstrated in the month of May, 1958.

upholstery leather was demonstrated to a group of tanners in the Institute in the month of May, 1958. The process is described below:

Details of the process demonstrated.

Raw materials.

45 bark tan cow hides of 5th quality weighing in all 508 lbs. were used.

Preparation for retannage: Splitting.

The tanned cow hides were trimmed (weight of trimmings 28 lbs.) and then soaked one by one in water for a minute and piled on a horse. They were then dry-drummed for 3 hours and split to 2·0 mm. thickness. By careful splitting, shaving was avoided. The weight of sammed (containing 50% moisture) grain splits was 486 lbs. and that of flesh splits 354 lbs.

Stripping and Bleaching. Next morning, grain splits were washed with 200% water for 10 minutes in a drum and then stripped with 2·5 lbs. of soda ash, containing 83·6% Na_2CO_3, (equivalent to 0·5% of the weight of the raw material taken) using a float of 150% and a duration of 10 minutes. The goods were then washed twice—first wash with 200% water for 10 minutes and second wash with 150% water for 5 minutes. Bleaching was effected with 2·5 lbs. oxalic acid, 2·5 lbs. sulphuric acid and 150% float; duration was 15 minutes. The bleached goods were washed with water.

Tanning:

Preparation of basic aluminium sulphate.

Basic aluminium sulphate was prepared the previous day using the following chemicals:

Aluminium sulphate: 70 lbs.
Sodium citrate: 5 lbs.
Soda ash: 17·5 lbs.

The sulphate and citrate were dissolved in 15 gallons of water taken in a tub and the soda ash was dissolved separately in 5 gallons of water. The soda ash solution was added in two or three instalments in course of an hour with good stirring. The solution was left to age overnight. The pH of the clear solution was 3·4.

Retanning:

After washing the bleached stock, 40 gallons of water were put into the drum and the entire tanning solution was added in bucketfuls with the drum running at 4 RPM. Drumming was for 45 minutes after which time 17·5 lbs. of soda ash separately dissolved in 10 gallons of water were added in three instalments within an interval of one hour and the drumming continued for another hour. Boiling test was applied to a piece of tanned hide taken from the thickest portion. No shrinkage was noticed. The actual shrinkage temperature of the tanned leather was found to be 112°C. The pH of the exhaust bath was 4·3. The tanned goods were then washed twice; first wash with 200% float for 10 minutes and the second wash with 150% float for 10 minutes.

Fat-liquoring. The composition of the fatliquor was as follows:—

Castor oil: 15 lbs. (3% on wt. of raw material)

Sulphated fish oil: 7·5 lbs. (1·5% on wt. of raw material).

Sulphated pongum oil: 2·5 lbs. (0·5% on wt. of raw material).

Soft soap: 1·25 lbs. (0·25% on wt. of raw material).

Borax: 5 ozs. (0·06% on wt. of raw material).

Water to make upto 10 gallons.

30 gallons of water were added to the drum containing the stock and the entire quantity of fat-liquor was added into the drum while running. Drumming was continued

for half an hour by which time the bath was almost like water. The liquor was then drained off and the goods dry-drummed for 30 minutes. The leathers were then taken out for setting and staking.

Setting and Staking. The leathers were then set out by machine and hung for drying. Next morning a second setting was done and the leathers were again hung up for drying. They were removed when still damp and after lightly wetting the dried portions with water using a brush, they were piled for an hour and then staked.

Buffing, snuffing, etc. Staked leathers were, next day, buffed on the flesh side using 80 grit paper and on the grain side with 320 grit paper. The leathers were then cleaned and trimmed.

Finishing.

Bottom coat of a light blue shade:

Composition:

White pigment (33% of solids): 8 lbs. 12 ozs.
Earnshaw Blue (33% of solids): 2 lbs. 14 ozs.
Yellow pigment (33% of solids): 6 ozs.
Bedacryl 188A (ICI): 12 lbs.
Water: 12 lbs.

The bottom coat prepared as above was padded twice on the snuffed side of the leathers and then allowed to dry.

Fixing: Two spray coats of the following fixing season were given.

Casein: 12 ozs.
Borax: 3 ozs.
Formalin 40%: 30 ozs.

The casein solution was diluted to 5% strength and added to the 10% formaldehyde solution.

Bottom clear lacquering. The leathers were then given two coats of the following clear lacquer.

Spartan clear lacquer: 1·2 gallons.
Spartan thinner: 3·6 gallons.
Total: 4·8 gallons.

1·2 gallons of this clear lacquer solution was used at this stage and the rest used later in topping. The leathers were found fast to dry rubbing and almost fast to wet-rubbing.

Pigment topping.

Composition:

Black Pigment: 1 lb.
Blue pigment: 1 lb.
Water to make upto 2 gallons.

Two coats of the above topping were sprayed on to the leathers carefully and then allowed to dry.

Printing and producing two-tone effect. The leathers were then printed using Antique grain and the pigment topping was rubbed off using a wet cloth, thus producing the two-tone effect. The leathers were then dried.

Fixing. Two coats of the formaldehyde fixing season were given.

Top clear lacquer. The remaining quantity of the lacquering prepared earlier was now used for topping thereby making the finished leather completely fast to dry and wet rubbing.

Measuring. The leathers were then measured, and smooth-plated to improve the appearance.

The finished leathers had an average thickness of 1·5 mm. and had all the qualities required of upholstery.

The process originally covered under a patent (Indian Patent No. 5316, dated 23-11-54, R. Selvarangan, and B. M. Das) has now been released to the trade free of cost.

TECHNICAL SEMINAR

Mechanism of Zirconium Tannage *

BY

T. S. RANGANATHAN

The first tanning experiments with zirconium, on a practical scale, were carried out about 25 years ago. Zirconium tannage was found to produce strong, through white leather of solid character with a fine nap on finishing for suedes. However, even as early as 1907, Garelli had observed that hide powder had some affinity for zirconium and thorium salts. The exact ionic state of zirconium in zirconium sulphate solutions and the mechanism of combination of zirconium salts with hide proteins have not yet been clearly understood. The present studies** are in this direction.

In the case of zirconium sulphate solutions, the pH of precipitation is very low, that is, 2·35; the tannage is, however, usually finished at a pH value of 4·0 to 4·5. Hence, several organic salts have been investigated with regard to their capacity in preventing such precipitation. Of these, only four—lactate, glycollate, citrate and gluconate—have been found to be effective masking agents. It is interesting to note that all these are salts of hydroxy acids. Whereas, it has been found, from ion exchange and electrophoretic studies, that zirconium exists mainly in the nonionic forms in solutions at room temperature, an addition of citrate converts cationic and nonionic zirconium complexes into the anionic ones.

* Summary of the Seminar talk delivered on 23-5-1958.

** Carried out at Leeds University.

From experiments carried out to elucidate the mechanism of zirconium tannage, using normal, deaminated and esterified hide powder samples and also hide powder treated with lyotropic salts, it would appear that zirconium is fixed to hide protein in the following two ways:—(1) by reaction of the uncharged amino groups of the protein with metal, forming a coordination complex and (2) the physical deposition of insoluble zirconium compounds. This view differs from that of Lasserre, who postulated that zirconium complexes were fixed in the main, to hide protein, by means of hydrogen bonds. The present studies would appear to indicate that anionic complexes of zirconium are ineffective as tanning agents and also in increasing thermal stability of hide protein.

If zirconium tannage is by the two processes postulated above, it appears to have, though metallic in character, more in common with vegetable tannage where fixation is envisaged to be through both amino groups and physical deposition. The observed similarity in mechanism, may well account for the close structural resemblances between these two types, even when observed under the electron-microscope. Further, zirconium tannage though metallic in character, can form round leathers of remarkable fullness, quite comparable to vegetable tanned material.

CLASSIFIED ABSTRACTS

RAW MATERIALS

EFFICACY OF FORMALDEHYDE FUMIGATION AGAINST SPORES OF BACILLUS ANTHRACIS ON HIDES. *Jyh-Jian Soong. J. Agr. Assoc. China (Taipei)* [N.S.], No. **15**, 48-59 (1956) (English Summary); *Chem. Abst.* **52**, 4221 (1958)—Spraying dry hides with 40% HCHO (**I**) was very effective against *B. anthracis* spores; 10-20% **I** was much less effective. The minimum exposure time was 17 hours for 17 ml. **I**/cu.m. and 6 hours for 22 ml. **I**/cu.m. Fumigation is carried out with a mixture containing 5 parts **I** and 3 parts $KMnO_4$ in tightly-closed chambers.

THE EFFECTS OF FORMALDEHYDE FUMIGATION UPON THE QUALITY OF HIDES. *Jyh-Jian Soong (Dept. Agr. Forestry, Taiwan). J. Agr. Assoc. China (Taipei)* [N.S.], No. **17**, 81-95 (1957) (English Summary) *Chem. Abst.* **52**, 4221 (1958)—Animals hides fumigated by spraying with HCHO solution after covering with paper were unaffected in their quality and ability to swell and absorb tannin. Direct contact spraying or submergence in HCHO damaged the hides.

PROCESSES PRIOR TO TANNING

IMPROVEMENT OF THE RAPID TANNING METHOD FOR SHOE SOLES. *P. I. Levenko. Legkaya Prom.* **17**, No. 3, 13-16 (1957); *Chem. Abst.* **52**, 1661 (1958)—Recipes are presented for the concentrations of the pickling baths, with respect to vegetable tanning agents, syntan AN, sulfite, bisulfite, also for NaCl and Na_2SO_4 in the chrome tanning bath.

VEGETABLE TANNING

INFLUENCE OF THE WATER ON THE YIELD OF TANNINS AND THE QUALITY OF THE TANNING EXTRACT. *A. I. Yakadin. Legkaya Prom.* **17**, No. 8, 16-17 (1957); *Chem. Abst.* **52**, 2439 (1958)—Extraction of oak wood with waters of hardness of 4·8 and 11·5 total, 2·2 and 6·5 permanent hardness (mg./1.) entailed losses of 3·2 and 11·6% of the tanning materials, respectively, through the formation of insoluble tannates as compared with the loss with the use of distilled water.

OTHER TANNAGES

THE IMPROVEMENT OF THE SWEAT RESISTANCE OF INSOLES. *D. Pettit, Australas. Leath. Trades Rev.* **54**, No. 1, 10 (1958)—The biggest enemy of footwear is perspiration and the brunt of attack by perspiration is borne by the insole. Therefore, the leather intended for use as insoles should possess in addition to the desirable qualities of lightness, strength, firmness, flexibility and good water absorption, an inherent chemical stability to perspiration. The major factors figuring in the breakdown of vegetable tanned leather by perspiration are (1) removal of water solubles disturbing the fixed tan/soluble tan equilibrium and leading to shrinkage of the leather and (2) neutralisation of the natural acidity of leather leading to loosening of the collagen tan bond and to oxidation of vegetable tans both fixed and soluble. Insoles, after use behave more like untanned hide than leather.

Development of insole tannage resistant to perspiration is dependent upon a suitable test to assess the performance of the tannages. The present paper describes results obtained in tests carried out with insoles of different tannages. Insoles of 9 different tannages —vegetable tannage (control), vegetable tannage with reduced water solubles, vegetable tannage treated with calcium oxalate, vegetable-syntan combination tannage, semi-chrome, semi-alum, full-chrome, chrome-syntan and chrome retan. Careful control was exercised during the tanning processes with weight, area and thickness checks kept on each piece so that the yield and the other characteristics of each method of tanning could be recorded. Chemical analysis and physical properties of all the leathers obtained were determined. The behaviour of the leathers obtained by the various tannages was compared both by laboratory tests with artificial perspiration and by a wear trial. The wear trial was carried out with the insocks cut out from the leathers. The laboratory tests consisted in wetting and drying cycles being carried out with solutions designed to have same effect as perspiration. Four liquids were used: (1) water, (2) a solution made up to represent human sweat concentrated 10 times, (3) concentrated ammonia and (4) a 24% solution of urea. The performance of the leathers in the wear trial was judged by changes in measurements of thickness, length and width of the insocks during wear, by changes in softness, stiffness, and grain crack resistance and by visual assessment of the amount of discolouration, distortion and cracking of the insoles. In the 'perspiration' tests, the performance was assessed by measurement of the changes in stiffness, softness, thickness, area and by visual assessment of the damage, that is, curling and darkening. The wear trial lays the tannages in the following order of resistance to perspiration.

full chrome and chrome syntan—very good;

semi-chrome and one chrome retan—good;

vegetable and semi alum—average;

vegetable-syntan, vegetable oxalate and

vegetable (reduced solubles)—all slightly worse than the normal vegetable tannage.

Chemical analysis of the worn insoles shows that most obvious changes in the wear took place in the water solubles.

Actually, in use, however, other factors, in addition to perspiration resistance, have to be taken into account—amenability to shoe making operations, yield, cost, etc.

V.S.P.

PROCESSES AFTER TANNING

LOWERING THE WATER PERMEABILITY OF RUSSIAN LEATHER. *V. N. Semenova. Legkaya Prom.* **17**, No. 9, 26-7 (1957); *Chem. Abst.* **52**, 2440 (1958)—Polyisobutylene dissolves in aliphatic and aromatic hydrocarbons and CCl_4 and swells in mineral and vegetable oils, but it does not absorb water nor swell in it. Leather was treated with a mixture of polyisobutylene (mol. wt. 85,000) 5·3, mineral oil 6·3, ozocerite 22, and paraffin 9·5. Addition of 25, 40 and 50 parts of the mixture/100 leather lowered the water permeabilities to 0·98, 0·91 and 0·29 ml./sq. cm./hr., respectively but air permeability remained constant at about 98 ml./sq. cm./hr. In further experiments hexamethylenetetramine was plasticized with a solution of gelatin and used as a dressing. With the decomposition of the former to HCHO and NH_3, the HCHO combined with amino groups of the gelatin and probably with the peptide linkages. Chains of the gelatin combined through CH_2 bridges, the micelle enlarged, and the viscosity rose, i.e., the leather became waterproof.

THE USE OF SYNTHETIC AND VEGETABLE TANNING AGENTS IN THE PRODUCTION OF CHROME LEATHERS: *K. M.Zurabyan, E. V. Kuz'mina, and A. I. Metelkin. Legkaya Prom.* **17**, No. 10, 25-6 (1957); *Chem. Abst.* **52**, 3380, (1958)—A 2-stage Cr. tanning process followed by a supplementary treatment with synthetic or vegetable tannins is recommended for upgrading sheep skins and hides of loose, porous structure. Among the synthetics used in experimental work were phenol-2-naphthol compounds, 'PS' and syntan 'SPS' (compositions not given), willow bark extract, and a fixer composed of phenol, $(NH_4)_2SO_4$, and HCHO. The hides are tanned for 6 to 8 hours in spent pickling liquor, with Cr_2O_3 equal to 0·6 to 1·0 % of the hide wt., pressed, sorted, shaved, weighed, and retanned at 35 to 38°, with Cr_2O_3 equal to 1·0 to 1·5 % of the shaved weight in liquor of 38 to 44 % basicity. After 1·5 to 2 hours alternate additions of Na_2SO_3 and Na_2CO_3 are made at 15-minutes intervals, up to 0·6 — 0·87 % and 0·2-0·4 % of the weight of the leather respectively. Dyeing and fatting operations follow. The synthetic or vegetable finishing tan is carried out for 45-60 minutes at 30-5° with an amount of tanning agents calculated to contain 1-3 % of tannin based on the weight of the semifinished product; pH 3·8-4·5. The usual finishing operations are employed. Thickness of hides so tanned are from 24 to 60 % greater than with single-stage Cr tanning. Quality is likewise improved by the removal of excess Cr in the final stage.

THE INFLUENCE EXERTED BY CHEMICAL PROCESS ON THE TECHNICAL PROPERTIES OF CHROME-TANNED SHEEPSKINS FOR SHOE UPPERS. *Gh. Havas and A. Minculescu. Ind. Usoara* (Bucharest) 4, 324-33 (1957); *Chem. Abst.* **52**, 3382 (1958) — Treatment with a Glyptal resin emulsion resulted in a considerable increase of the tensile and tearing strengths of the sheepskin leathers.

IMPREGNATION OF HIDES WITH AQUEOUS DISPERSIONS OF POLYMERS. *K. M. Zurabyan and S. A. Pavlov. Legkaya Prom.* **16**, No. 4, 32-8 (1956); *Chem. Abst.* **52**, 50-13 (1958) — Recipes are presented, illustrated by photomicrographs, for impregnating hides with Me acrylate **(I)**, **I** plus dibutylphthalate, or **I** plus Bu acrylate plus methacrylic acid, dispersed in gas oil, with Emulsifier MK or Nekal VKh and an unspecified stabilizer. The dispersions have pH values between 2 and 3. It is possible in this way to prepare hides which contain up to 30 % of a polymer or a polymer mixture from goat and calf skins.

IMPREGNATION OF SOLE LEATHER. *Ch. Gastellu, M. Giroflier and G. Desjours, B.A.F.C.I.C.*, **19**, 255 (1957).

In earlier work, samples of vegetable and chrome vegetable bends were impregnated with synthetic rubber, i.e., polyisobutylene. The seasoned but not rolled leather was immersed in a solution of the synthetic rubber for 24 hours. The leather absorbed 7·7 to 12 per cent of the elastomer. Lesser quantities were absorbed by the butt portion, the absorption being stronger in portions adjoining the shoulder and bellies. Impregnation resulted in amelioration of the quality of leather, that is, the absorption of water and resistance to wear. This amelioration is particularly effected in the bend portions adjoining the shoulder and the bellies, so much so, the impregnation has the effect of rendering the leather more homogenous and in raising the two coefficients, namely, coefficient of resistance to wear, and coefficient of impermeability to water. The leathers thus prepared were used in fabricating shoes in order to verify whether they lend themselves to the normal shoe making operations. The method has been now extended, in that an apparatus has been designed for treating a dozen bends at a time. The improvement in the quality is as follows :

> Degree of resistance to wear 78 % in shoulder region, 74 % in the bellies and 69 % in the butt with vegetable tanned leather and 57%, 42% and 28% respectively with chrome vegetable tanned leather.

Improvement in the impermeability (after soaking for one hour) is as follows :

> Shoulder region 29%, Belly 46% and butt 40% with vegetable tanned leather and 40 %, 45 % and 48 % respectively with chrome vegetable tanned leather.

Experiments have been carried out with a large number of other producs also, and it has been found that a product which improves resistance to wear is without appreciable effect as regards impermeability and vice versa.

—*V.S.P.*

THEORIES

THE STRUCTURE OF ARTIFICIAL SHOE-SOLE LEATHER PRODUCED WITH LEATHER FIBRES. *G. I. Kolossova, A. I. Badanina and S. A. Pavlov, Tsentral Nauch-Issledovatel. Inst.*

Zamenitelei Koshi **1954**, No. 6, 28-38; Referat. *Zhur. Khim.* **1956**, Abstr. No. 8659; *Chem. Abst.* **52**, 769, (1958)—Microscopic examination to elucidate the components, bonding, and distribution in sole board and other materials made from leather fibres, is described. Since these materials contain dark-coloured components (carbon black, etc.) the study is conducted on specially prepared samples, gradually more complicated until they reach the proper formulation. The separate elements of the structure are selectively dyed. For the leather fibres, it is recommended to use hematoxylin, safranine, acid fuchsin, eosin, hematein, methylene blue, etc. For dyeing the rubber, Sudan III is used. The methods for cutting and dyeing the slices are given. For study of the mutual distribution of the fiber and the binder, one of them is destroyed and washed off. Since it is impossible to remove the vulcanized rubber without destruction of the leather fibres, the fibres are destroyed by a mixture of H_2SO_4 and $K_2Cr_2O_7$. The leather sections are cut horizontally (parallel to the surface of the board) and edgewise. It is shown that sole board and plastic leather are multilayer materials the structure of which may be considered a single network composed of rubber and fibres, the rubber being deposited on the fibre surface forming a frame. Judging by the lengthwise and crosswise cuts, the layers in the materials formed on rolls are wavy, while in the board they are stretched more. The thickness and stretching of the plastic leather layers depend on their different speeds inside the sheet when passing through the rolls. It is assumed that by changing the spacing of the layers and also the fibres inside the layer, it would be possible to produce artificial leather with improved properties.

RAISING THE WATER RESISTANCE OF PROTEINS. *S. A. Pavlov and E. K. Pogosyants (Moscow Tech. Univ. Light Ind., Moscow). Nauch. Trudy MTILP* **4**, 3-31 (1954); *Chem. Abst.* **52**, 1661 (1958).—Ac_2O blocks active goups of gelatin. Amino N in gelatin is lowered from 4·3 to 0·99 %. Ketene lowers it to 2 %. The acetylation of gelatin by Ac_2O is therefore more effective. Acetylation of gelatin films by ketene makes them more resistant to H_2O and acids than does acetylation by Ac_2O. Diketene is probably bound. Gelatin films after treatment with Ac_2O or ketene shrink in boiling water and do not dissolve. The treatment of gelatin by Me_2SO_4 leads to N-and D-methylation, and perhaps to a direct combination with peptide bonds, but the resistance of gelatin against H_2O is not raised. The highest resistance of gelatin against H_2O is imparted by cross linking agents, e.g. HCHO. The tanning effect is signalized by the raising of shrinkage temperature and can be attained by agents capable of forming 3-dimensional structures. The existence of cross links in tanned proteins has been experimentally proved. In acid medium, HCHO forms CH_2 cross links not only between neighbouring amino acid residues but also between different mols. Cross-linking between peptide links is, however, not probable. The previous treatment of gelatin with Ac_2O does not influence the binding of HCHO. By the HCHO treatment, 3·24% of amino N in gelatin is blocked.

PERIODIC DEFORMATION OF COLLAGEN IN SOLUTIONS OF ELECTROLYTES AND TANNING AGENTS. *A. G. Pasynskii and A. M. Țongur* (A. N. Bakh Inst. Biochem., Acad. Sci. U.S.S.R. Moscow); *Kolloid, Zhur.* **19**, 483-9 (1957); *Chem. Abst.,* **52**, 3381 (1958).—On periodic deformation with a frequency of 1 to 1000 cycles/min. leather behaves as an elastic protein gel in water and diverse solutions (2*M* NaCNS, KCNS, LiCl, 5*M* urea, 25% $(NH_4)_2SO_4$ at temperatures below the shrinkage point as well as at the various stages of the technological process and possess only small relaxation periods. Only chrome-tanned leather (before the stage of vegetable tanning) possesses a large relaxation period that in the histologically heterogenous porous structure makes its appearance despite the fixed position of the molecules. This effect was used to accelerate the penetration of the tanning agent into the collagen. The tanning process could be considerably accelerated in comparison with tanning under plant conditions by subjecting the chrome-tanned leather to periodic compression in the tanning solutions with a frequency corresponding to the large periods of relaxation.

WET HEATING OF COLLAGEN. *N. N. Stefanovich* and *A. N. Mikhailov (Central Sci. Research Institute Leather and Shoe Ind. Moscow)*. *Kolloid Zhur.* **19**, 741-6 (1957); *Chem. Abst.* **52**, 5014 (1958).—Raw hide (**I**), limed hide (**II**), and leather tanned with phosphotungstates (**III**) were heated in H_2O at 63-6° for 10 minutes. The resulting collagen had heat capacity (0·31-0·48 cal./g.) identical with that before heating. The difference between the heat effects on immersing heated and nonheated collagen in H_2O at 74° was 1.9, 3·6 and 3·8 cal./g. for **I**, **II**, and **III** respectively, i.e., similar to the heat of protein denaturation rather than to that of melting. An agreeing value was calculated from the heating curves of heated and nonheated collagen.

TESTING

NEW METHODS OF ANALYSIS. *Alexandra Petrovici. Ind. Usoara* (Bucharest) **4**, 288-90 (1957); *Chem. Abst.* **52**, 767, (1958). Analytical methods used in the leather industry are reviewed. The free acidity of tanned leather is determined by extraction with Na acetate in glycol and propionic acid solution followed by potentiometric titration.

COLORIMETRIC METHOD FOR DETERMINING DIALDEHYDE CONTENT OF PERIODATE-OXIDIZED STARCH. *C. S. Wise and C. L. Mehltretter, Anal. Chem.* **30**, 174 (1958). Micro quantities of periodate oxystarch have been determined colorimetrically. This rapid method is particularly suited to the precise estimation of low percentages of carbonyl groups in periodate-oxidized starches. A p-nitrophenylhydrazone of oxystarch is precipitated from aqueous solution, dissolved in ethyl alcohol, and determined spectrophotometrically.

ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF SULFATE, CHLORIDE, AND FLUORIDE WITH CHLORANILIC ACID. *R. J. Bertolacini and J. E. Barneyii, Anal. Chem.* **30**, 202 (1958). The intense absorption of solutions of chloranilic acid in the ultraviolet region provides the basis for the spectrophotometric determination of trace amounts of sulfate, chloride, and fluoride. Sulfate is determined by reaction with barium chloranilate in 50% ethyl alcohol, buffered at pH4 (absorption measured at 332 mμ); chloride, with mercuric chloranilate in 50% methyl cellosolve, 0·05N in nitric acid (absorption measured at 305 mμ); fluoride, with strontium chloranilate in 50% isopropyl alcohol, buffered at pH_4 (absorption measured at 332 mμ). Limit of detection is 0·06 ppm. for sulfate, 0·05 ppm. for chloride and 5 ppm. for fluoride. The procedures for sulfate and chloride provide greater sensitivity, with fewer interferences, than currently available methods. The procedure for fluoride is subject to interference from most anions but rapid in limited routine uses. The method can be applied to other anions.

ASCENDING CHROMATOGRAPHY OF POLYPHOSPHATES. *George G. Berg, Anal. Chem.* **30**, 213, (1958). Variables involved in the chromatographic analysis of polyphosphates were surveyed in terms of their effect on R_f values. The variables included selection and concentration of components of solvent, composition of atmosphere, and condition of paper. An ascending method provided constancy of experimental conditions and permitted control of R_f values in terms of three properties of the solvent: choice of alcohol, amount of water, and pH. Isopropyl alcohol solvents were suitable for lower polymers only. Data on chromatographic identification of higher polymers by other solvents were obtained.

APPARATUS FOR CONTINUOUS ELECTROCHROMATOGRAPHY. *Harold H. Strain, Anal. Chem.* **30**, 228 (1958). A simple, efficient, adaptable, and economical apparatus has been tested for continuous electrochromatographic separations. The stabilization medium for the flow of the background electrolytic solution and concomitant transverse electrical migration is a tapered sheet of soft, thick industrial filter paper. The support for the paper is a block of solidified polystyrene foam. Evaporation of the background electrolytic solution is prevented by the polystyrene foam support and by a loose curtain of polyethylene sheeting. This apparatus has been utilised for the continuous separation of various inorganic ions.

ION EXCHANGE PAPER IN RAPID SEPARATION AND IDENTIFICATION OF BASIC AMINO ACIDS. (Arginine, Histidine, and Lysine from Casein Hydrolyzates.) *Murray M. Tuckerman, Anal. Chem.* **30**, 231 (1958). A newly available sulfonic acid-type cation exchange resin paper allows separation of arginine, histidine, and lysine from Casein hydrolyzates in 90 minutes. A pH 5·2 acetate buffer is used as the developing solvent in conventional descending chromatography technique.

MICRODETERMINATION OF VOLATILE ALDEHYDES. *Irving R. Hunter and Earl F. Potter, Anal. Chem.* **30**, 293 (1958). In the microdetermination of volatile aldehydes, particularly those generated by and distilled from ninhydrin oxidations of amino acids, the aldehydes are absorbed in and made to react with an excess of sodium bisulfite to form stable complexes. Excess bisulfite is removed by oxidation with iodine. A measured amount of iodine in excess of the aldehyde-bisulfite equivalent and an alkaline buffer are added to the residual aldehyde-bisulfite complex. The iodine quantitatively oxidizes the bisulfite and aldehydes. Excess iodine is then determined by back-titration with standard thiosulfate. A blank is run at the same time and the difference in titration values is used to calculate aldehyde equivalent.

BYE-PRODUCTS

(MEANS FOR) SECURING THE PROPER PURIFICATION OF WASTE WATERS FROM TANNERIES. *A. A. Usacheva. Legkaya Prom.* **17**, No. 10, 17-21 (1957); *Chem. Abst.* **52**, 3381 (1958). The nature and composition of typical wastes from the various tanning processes (chrome, synthetic, and vegetable) are described, and the general methods of sedimentation are taken up. Grossly contaminated tannery waste waters may contain 20,000 ppm. suspended solids. Basic minimum construction recommended includes a battery of screens with meshes of 10 $\times$ 20 mm., a continuous sedimentation system with flow not greater than 20 mm/sec. and a detention period of not less than 5 minutes and a closed sludge tank provided with drainage.

BY-PRODUCT UTILISATION POTENTIALS. *Fred O'Flaherty, Leather Manufacturer,* **75**, No. 1, 5, (1958). In the tanning industry, there are a number of by-products which have proteins in common. In assessing the commercial utilisation possibilities of these, the economic aspect has to be taken into account. A chicken feed supplement made from limed hide fleshings and an animal feed supplement made from green cattle fleshings and hide trimmings have good economic possibilities whereas some plastics made from fleshings and a detergent also made from fleshings do not offer an attractive return.

Protein hydrolytic products have been considered as foaming surface active agents and textile adjuncts. The general method is to use the hydrolysate condense it with fatty acids and sulphonic acids. Products suitable for fire fighting and as flotation materials have been used. However, these are not of interest since cheaper proteins are available. By reaction of protein hydrolysates with a number of materials, products have been obtained which could be used as fungicides, bactericides, herbicides (weed killers), chelating agents, detergent soil stabilizers, rubber accelerators, nematocides and insecticides. So, most of these materials have application in the agricultural field. Some of the other potentially profitable developments for the tannery by-products are the following :—

Amino Acids (These will find use in nutrition and also in the synthesis of materials like polyvinylpyrrolidone); chemi biotics; protein base paints; special purpose protein sheets; plant growth substances to apply to leaves; glue derivative stiffener for fabrics;

a better gelatine; a better glue; leather as filter bed; an additional application in the field of plastics; paper coating; roofing material; light aggregate for concrete; hydrolysate and betaines from sugar as delimer.

V.S.P.

PATENTS

TANNING AGENTS. *Societe anon. des manufactures des glaces et products chimiques de St. Gobain, Chauny & Cirey Fr.* 996, 642, Dec. 24, 1951; *Chem. Abst.* **52**, 770 (1958). Stable tanning agents for leather having a SO_4: Fe ratio of 1:1 and a pH of 2·5-3·0 are made from raw $Fe_2(SO_4)_3$ solution. The free H_2SO_4 is neutralized with a base, e.g. slaked lime, leaving a product with a SO_4: Fe ratio of 1·5:1. A base or basic salt is then added together with tartaric acid to precipitate 1/3 of the sulfate ions remaining in solution. The tartaric acid can be added before the initial neutralization. Preferably, 1 mole is added per g. atom of Fe. A complex, $SO_4FeOCOCH(OH)CH(OH)COOH$, is obtained. Maleic acid may partly or entirely replace the tartaric acid. The solution is then filtered and a base, e.g. NH_4OH, is added to raise the pH to 2·5-3·0 and give a soluble salt with the complex. By rapid evaporation of the solution in a thin film or as a spray, a water-soluble product is obtained.

SYNTHETIC TANNING AGENTS. *Josef Mahler & Co. Kommandit-Gesellschaft chem. Fabrik u. Gerbstoffe, Spezial-produkte fur Lederveredlung (Karl Similicki, inventor). Austrian* 193, 533, Nov. 25, 1957; *Chem. Abst.* **52**, 1662 (1958). Sulfite liquor is treated with Al and (or) Cr sulfates, the precipitated $CaSO_4$ filtered off, and water-soluble sulfonated condensation products of HCHO with monophenols and (or) naphthols are added to the filtrate. Preferably, approximately 10-15 parts by weight (of dry substance) condensation product is added to 45 parts by weight sulfite waste liquor. Condensation is effected either before or after condensation with HCHO.

PREPARATION OF HIDES FOR TANNING. *Paul Lecompte and Joseph Delecourt. Fr.* 1,023,228, Mar. 16, 1953; *Chem. Abst.* **52**, 1662 (1958). The cells of raw hides are emptied of their organic matter and then filled with an imputrescible product, e.g. rubber. A treatment with a bath containing 0·5% crude pork

pancreas powder and 5% NH_4Cl at 25-30° opens the cells and empties them. It is followed by a histological fixation with a solution containing 1% HCHO, 0·1% Na_2CO_3, and 0·2% NH_3 at 25° and by filling the open cells by immersion in a latex bath. This bath should contain 20% globular rubber and is prepared by pouring commercial ammoniacal latex with 0·1% trypsin added to a K resinate solution; NH_2OH is added for sterilization. When synthetic latex is used, no trypsin and NH_2OH are added. After a coagulating wash with a Cr salt, the leather is tanned by conventional methods. The leather is thus obtained in 25-40% greater thickness and in sensibly better yields than by the usual treatment.

SORBENT FOR THE QUANTITATIVE DETERMINATION OF TANNINS. *P. Ya. Frenkel and A. N. Mikhailov. U.S.S.R.,* 106, 764, Aug. 25, 1957. *Chem. Abst.* **52**, 3382 (1958). A powdered sorbent for use in the analysis of tanning agents as well as industrial liquors is obtained by the partial hydrolysis of the acid-soluble polyamide capron followed by recrystallisation.

WATERPROOFING OF LEATHER. *E. K. Maminov* and *M. G. Voronkov. U.S.S.R.,* 107, 334, *Sept.* 25, 1957. *Chem. Abst.* **52**, 3382 (1958). The water resistance of leather is improved by saturation with organic Si compounds which harden in the presence of 0·01% of a $TiO(OH)_4$ ester. Solutions (4-5%) of silanes of the general formula $RSi(OAc)_2OCOR'$ are used, where R' is an alkyl radical containing more than 10 C atoms. The silane is dissolved in an organic solvent.

GENERAL

NEW HORIZONS IN LEATHER TECHNOLOGY. *Fred O'Flaherty and J. J. Tancous, Australas. Leath. Trades Rev.* **54**, No. 3, 14 (1958). The authors try to penetrate the future in Leather Technology and Industry developments.

Today, the tanner can purchase hides which are fleshed at the time of flaying and cured in a brine disinfectant bath. Tailor-made sides with green fleshing and brine cured are also available.

Soaking: There is a considerable possibility that in the next century, we shall see solvent processing adopted. This means that if the hides and skins are put into the white stage by the packer using some of the new solvent fat extraction and dehydration processes, the tanner will receive a hide or skin ready for solvent processing.

Unhairing: The future unhairing will be done by the packer. It will be done before the manure on the animal has time to cause value reducing stains and grain damage. These important process changes could result from improvements and developments in unhairing with enzymes. The future will see machines with compressed air and electronics which will do the whole job in short order. The machine will so mechanically wash the stock that soaking will be rapid and uniform, the chemicals used will unhair in hours and no one will touch the hide from the time it is fed into the machine; only it comes out white pickled and possibly dehydrated.

Bating: We shall again see new enzymes. With time saved in the preparation processes and with simultaneous alteration of the skin collagen to give new and wanted properties to leather the bating process will be just another part of the work done by the beam-house machine.

Pickling: When the tanning industry gets geared to a better tempo later in the present century, pickling will not be needed, the skins and hides will be degreased and dehydrated, in one operation. Automation is seen in the continuous processes, bating, pickling and tanning.

Tanning: Replacement tannins are now available. Solvent processing is well-established in several pilot scale plants and in regular production in one tannery. In future, such high-priced materials as skins and hides will be accorded treatment in keeping with their value. We can visualise skins and hides being put into a white pickled state by the packer and that there would be several new uses for hide substances other than making leather. The leather to be made would be different too. The hides would be treated chemically to give them new and wanted properties before tanning.

Fatliquoring and stuffing or currying: The years of tomorrow will bring another line of leather lubricants; silicones, silomanes, and their combination with acrylates will be the materials used. Even now there are tailored-to-order materials which will not only give lubrication and water repellency to leather but will provide

the fullness which now is obtained from vegetable tanning materials.

Finishes: Leather of hundred years ago looked, smelled and felt like leather. The leather of the next hundred years will be distinctive and will capitalise on all the natural and inherent properties and characteristics of skins and hides. Leather in the next hundred years will be so made that it will fit hundreds of new uses.

The future will see electronics doing most of all the control work in the tannery. Electronics will be a tool of quality control, it will mean more uniformity and a more profitable leather business.

V.S.P.

NOTES & NEWS

Tanning—a most promising application of Dialdehyde Starch

Dialdehyde Starch's brightest future seems to be in leather tanning, especially for making garment leather. Early tests show some advantages, say USDA chemists at the Eastern Regional Research and Development Division, where tanning studies have been made. Among these are light colour of tannage and stability on the alkaline side of the isoelectric point of collagen. For tanning, more than half of the glucose units are oxidised.

Chem. & Eng. News, **35**, No. 49, 59 (1957).

Tannery waste useless for Horticulture

The idea that tannery sludge waste might find widespread use as a garden mulch for vegetable crops has been discounted.

An agricultural experimental station in the US has been doing some research on the subject, and has found that the waste has an unfortunate toxic effect on the soil. Vegetables planted in sludge-treated soil died before they were fully grown, which was due to the large amount of boron found to be present.

—*The Australian Leather Trades Rev.* **54**, No. 1, 19 (1958).

Eastman 910 Adhesive

Eastman Chemicals new liquid adhesive sets without heat pressure evaporation of solvent or long curing time. It can be used with all sorts of materials. Adhesive action results from the polymers of a cyanoacrylate monomer. The adhesive is composed of about 90% monomer and 10% thickening agent, stabilizer and plasticiser. A catalyst also is used. However, the catalyst would be needed only for practically instantaneous bonding or for materials which would otherwise be difficult to bond, for example, acid-washed metals, certain types of wood and *leather* and other materials of acidic nature. Quick set time and high strength are two of its important virtues. It can find uses where there is need for fast set and cure, bonding of materials which do not normally

respond to available adhesives and high bonding strength at small joining surfaces.

Generally, the bond has good solvent resistance. Immersion in organic solvents like alcohol, benzene or acetone for even 24 hours has not much effect. Weak alkaline solutions weaken the bond, weak acids have lesser effect. Prolonged exposure to high humidity and temperatures weakens or destroys the bond.

—*Chem. & Eng. News*, **35**, No. 42, 56 (1957).

Export Prospects with West Germany

Germany imports substantial quantities of finished leather from the UK, France and other countries. A large quantity of bark tanned goat skins is imported into Germany both direct from India and via London. These skins are dressed by German tanners and mostly used for shoe lining and certain qualities of uppers. If some effort is made, there is a possibility of exporting East India and tanned hides to Germany. A regular business can be established for kip linings manufactured from Indian tanned hides if taken up by some tanners. There is also a market for lining leathers in goat and sheep skins, if competitive prices are to be quoted. In regard to other leather goods, it is stated that patterns, designs and colours are changed almost every season. However, a beginning can be made in the export of such articles as wallets, portfolios, etc., where the changes in design are not many, by manufacturing them according to the designs and sizes required by the trade in Germany. In the export of leather goods, care chould be taken to use superior quality locks, zip fasteners and other fittings.

—*J. Ind. & Trade*, **8**, 11 (1958).

Russian Shoe output rises 90% over 1955 figures

Soviet Russia increased her production of leather footwear markedly during the past two years to a total of 179,660,000 pairs in 1957. This is estimated by Julius Schuitzer, Director of the leather shoes and allied products division of Department of Commerce, U.S.A. The gain from 1955, the last time a similar survey was made, was 85,660,000 pairs or 90% of the 1955 output in the Soviet, of 94,000,000 pairs, according to Schuitzer's figures.

The Soviet gain accounted for two thirds of the total increase of 125,194,000 pairs during two years for leather footwear output in all European countries.

The Soviet figures reflect emphasis on output of consumer goods. The Schuitzer figure is less than the Russian figures.

The total production for Europe in 1957 is reported at 671,917,000 including Russia, compared with 546,723,000 pairs in 1955.

Czechoslovakia had production of 15,860,000 pairs two years ago and dropped to 15,500,000 in the year 1953.

Hungary had production of 4,000,000 pairs in 1955 and dropped to 3,983,000 pairs.

Rumania had production of 2,600,000 pairs in 1955 and dropped to 2,500,000.

Virtually all other 24 countries had gains, the figures show. Here are the figures for 1955 and for 1957.

Foreign output of Leather Footwear in Million of pairs

		1955	1957
Austria	..	8,600	9,250
Belgium	..	9,200	9,310
Czechoslovakia	..	15,860	15,500
Denmark	..	6,312	6,800
Ireland	..	5,100	5,750
Finland	..	3,200	3,760
France	..	52,000	56,200
Germany (West)	..	75,000	79,620
Greece	..	6,000	6,730
Hungary	..	4,000	3,983
Italy	..	40,000	44,814
Netherlands	..	16,645	18,200
Norway	..	4,200	5,200
Poland	..	6,250	6,500
Portugal	..	3,000	4,220
Rumania	..	2,600	2,500
Spain	..	19,500	24,500
Sweden	..	11,350	13,250
Switzerland	..	9,000	11,610
U.S.S.R.	..	94,000	179,660
U.K.	..	144,300	152,000
Yugoslavia	..	6,600	7,150
Other	..	4,006	5,410
Total	..	546,723	671,917

—*Leather & Shoes*, 135, No. 14, 34 (1958).

Sweden Imported 1·3 million pairs in 1957

New orders and employment in the Swedish Leather Industry were fairly satisfactory in 1957, according to the annual report of the Swedish Leather Association. The output during the year was up by eight per cent to 11 million pairs. (Sweden's population is over seven million).

The number of lighter and simpler models of shoes increased. The proportion of ladies shoes also continued to rise.

Shoe imports, which showed some decline in 1956, rose heavily in 1957 and totalled 1·35 million pairs, or some 12 per cent of the domestic output.

The shoe retail trade continued to increase in 1957 and sales went up by three per cent in value. The number of pairs sold rose by 350,000, while the retailers stocks in hand at beginning of 1958 were over 400,000 pairs larger than a year before.

—*Leather & Shoes*, 135, No. 12, 15 (1958).

Shoe Manufacturers Seek Government Help

Mr. A. N. Verma, President of the Agra Shoe Manufacturers' Association, asked the Government for more assistance for development of the shoe industry.

Mr. Verma, who was addressing at the sixteenth annual general meeting of the association on April, 17, demanded that a seasoned-wood last factory should be opened at Agra. He said that large quantity of foreign demands were coming for the hand-welted shoes and it was necessary hat a seasoned-wood last factory was opened here to maintain quality.

He also demanded a 25 per cent depreciation on wooden lasts so that the manufacturers may get legitimate relief.

Mr. Verma referred to the Small Industries Service Institute and asked the manufacturers to take fullest advantage of the services of the shoe experts through this institution. He advocated a rational introduction of machines to cope with the increased foreign demand.

During the past year, about 80,000 pairs of shoes, at a cost of about Rs. 14 lakhs, were supplied to foreign markets, specially the Soviet Union and Poland.

'Unfortunately', Mr. Verma added, 'the type of shoes demanded by the Polish inspector was different from those which were got prepared by the corporation. This resulted in non-acceptance of about 12,000 by the buyers, which normally would have been returned to the trade involving untold loss and hardship'.

He disclosed that a two-man screening committee has been constituted with one representative each of India and Poland to sort out shoes which were according to the samples.

—*National Herald*, 23-4-1958.

Training in Leather Industry

The Government of India has approved a scheme for the establishment of a model training and production centre in hide flaying, curing, carcass and leather utilisation, and tanning at Bakshi-ka-talab, Lucknow. The scheme provides for setting up of three sections at the centre. One of them will be for hide flaying, curing and carcass utilisation; the second for tanning; and the third for footwear and leather. The object is to train instructors for schools to be set up in the States. These instructors will further train 'charmalaya' workers and act as supervisors in the industry. It is expected that the centre will train 100 students each year—60 for hide flaying and 20 each for tanning and footwear. The selection of the students will be made on an all-India basis. The scheme is expected to cost Rs. 17·46 lakhs. Of this, the Government of India will contribute Rs. 8·47 lakhs. The Netherlands Government has also agreed to send three experts—one for each section—and equipment for the centre at a total cost of Rs. 8·12 lakhs.

—*Eastern Economist* 25-4-1958.

RESEARCH BEARS FRUIT

Practical Demonstration No. 3

(Second Series)

Process: Manufacture of Full Chrome Glazed Kids.

Period: 18th June to 23rd July, 1958.

Place: Central Leather Research Institute.

The next in the second series of practical demonstrations will be on the manufacture of Full Chrome Glazed Kid.

Glazed kid is a high class leather manufactured from goat skins by chrome tanning process for making high class ladies' shoes, handbags, fancy articles etc.

India produces about 22·5 million pieces of raw goat skins annually and nearly about 80% of this valuable raw material is being exported in raw state mainly to U.K. and U.S.A. fetching about 70 million rupees. If instead, these raw goat skins are converted into finished glazed kids in India, and exported the value of this industry will be trebled.

You recall that the process for the manufacture of glazed kid was demonstrated in June, '57. A number of tanners participated in these demonstrations and they are following up this process in their tanneries. Since that time, there have been a number of enquiries from the industry for details of this process. Additional researches have since been made on the manufacture of glazed kids using indigenous materials and hence it is proposed to demonstrate this process in the month of June, '58. If you are interested in this line of work, you are most welcome to send your representatives to get trained in the manufacture of glazed kids. You may kindly intimate the names of the representative(s) who are likely to attend this demonstration. After following the demonstration, we would request you to try this process in your tannery and give us your valuable comments.

Practical Demonstration No. 4

The manufacture of vegetable tanned sole leather.

C. L. R. I. NEWS

1. M. Albert Mirles, Chemical Engineer, Department of Economic Affairs, Government of France visited the Institute on 12th May, 1958, and had discussions regarding the Pilot Plant Projects with the concerned Officers. Dr. B. N. Mitra, Assistant Director-General, Council of Scientific & Industrial Research also was present.

2. Dr. Y. Nayudamma attended the meeting of the Forest Utilisation Board of the Government of Madras held at Ooty, from 9th to 11th May, 1958.

3. Shri T. Gopinath has been appointed as Senior Scientific Assistant with effect from 14th May, 1958.

VISITORS

Name	*Date of Visit*
1. M. Albert Mirles, Chemical Engineer, Department of Economic Affairs, Government of France	12-5-1958
2. M. Georges J. Graf, Trade Commissioner of France in Madras	

Editor Y. Nayudamma. Published by N. Subramanian, on behalf of the Central Leather Research Institute, Adyar, Madras-20. Printed by G. Srinivasachari, B.A., at the G. S. Press, 21, Narasingapuram Street Mount Road, Madras-2.