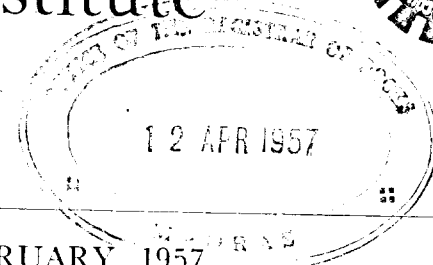


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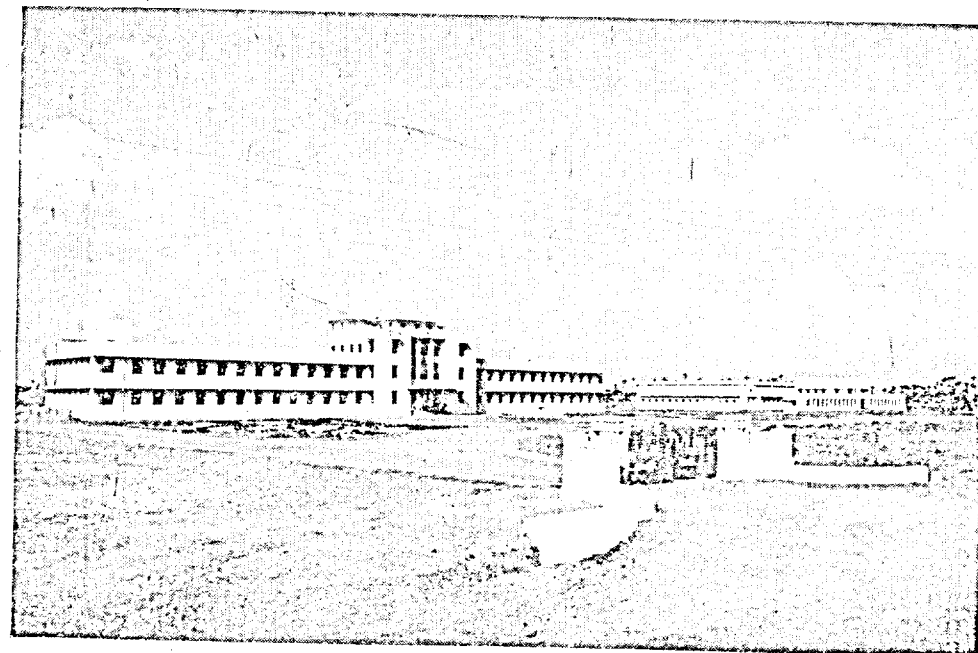
Bulletin of  
The Central Leather  
Research Institute  
Madras



VOL. III

FEBRUARY, 1957

No. 7



COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH  
INDIA

# Bulletin of The Central Leather Research Institute

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Vol. III

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No. 7

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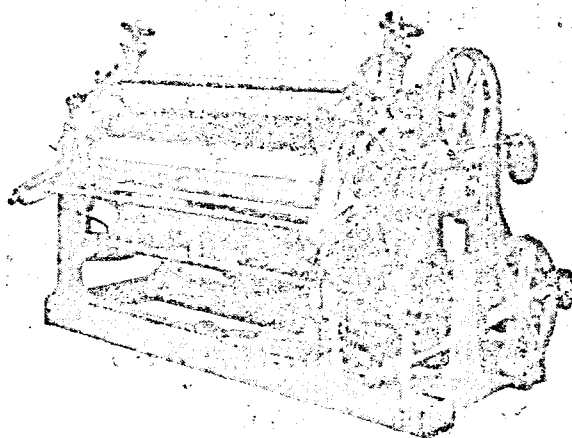
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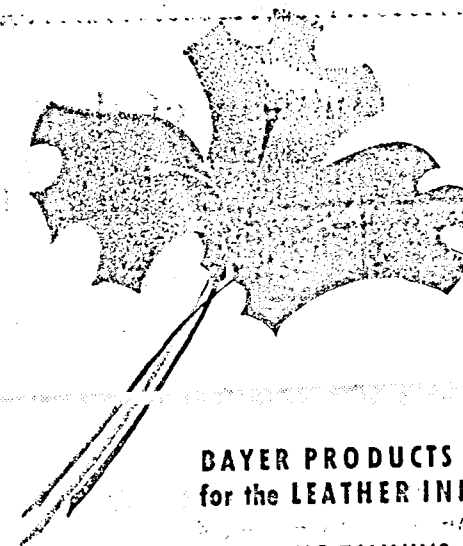
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**CENTRAL LEATHER RESEARCH INSTITUTE,**  
**ADYAR, MADRAS-20.**

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**A NOTE ON THE NATURE OF TANNINS FROM THE  
CASUARINA TREES**

*C. equisetifolia* is characteristically a seashore "large ever-green tree with a straight cylindrical bole, the ultimate branches being slender, cylindrical, jointed and green, with leaves reduced to minute scales." <sup>1</sup> Under favourable conditions, the tree attains a height of 100 feet and more, and a girth of 5 feet.

The vernacular names of the tree are as follows :—

Tamil — Savukku  
Telugu — Sarugudu, Chavukku  
Kanarese — Sarve Mara, Chabaku  
Malayalam — Chavukku  
Hindi — Jangli Saru  
Bengali — Jau  
Marathi — Suru  
Gujerathi — Vilayathi Saru

The tree is commonly known as Casuarina tree.

The tree thrives best and occurs wild in abundant sunlight on loose sandy soils near the shores at the head of the Bay of Bengal, Burma and Andamans.

Casuarina plantations are worked out very successfully in North Kanara, Nellore and also in the Bombay State.

The Casuarina bark is astringent and it contains a catechol type of tannins.

It was thought worthwhile to evaluate the tannin content of the Casuarina tree and to test its tanning action on hides and skins. The complete tannin analyses of the Root and the Bark of the Casuarina tree by the Official Method are given below :—

TABLE NO. I

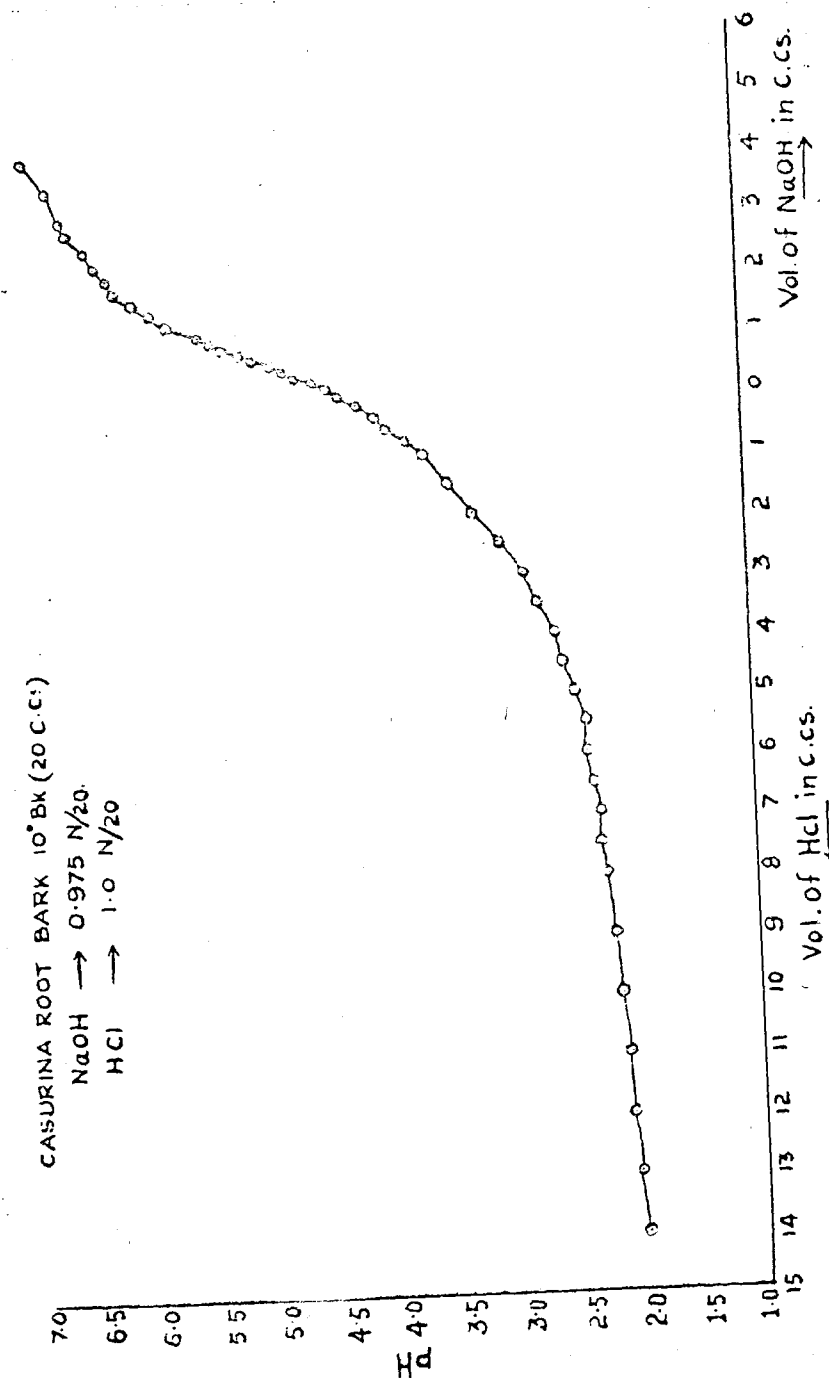
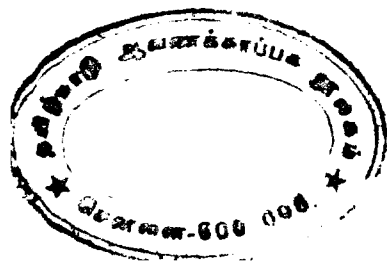
ANALYSIS OF THE CASUARINA BARK AND THE CASUARINA ROOT.

| Type of tannins                  | Root Bark<br>Catechol | Bark<br>Catechol |
|----------------------------------|-----------------------|------------------|
| % of Moisture                    | 12.4                  | 12.2             |
| % of Total solubles              | 19.47                 | 12.82            |
| % of Soluble Non-tannins         | 4.52                  | 2.8              |
| % of Tannins                     | 14.95                 | 10.02            |
| T/N.T. Ratio                     | 3.3                   | 3.6              |
| % of Total Ash                   | 1.6                   | 1.4              |
| Color of the Analytical Solution |                       |                  |
|                                  | R 5.1                 | 3.5              |
|                                  | Y 10.7                | 12.0             |
| pH of the Analytical Solution    | 4.65                  | 4.8              |
| % of sugars (as d-glucose)       | 2.65                  | 1.4              |
| Salts of weak acids              |                       |                  |
| Mg. equ/100° Bk/litre            | pH                    |                  |
|                                  | 2.8 87.5              | 175.0            |
|                                  | 2.0 350.0             | 700.0            |
| Acids                            | 5.8 29.75             | 59.5             |

The Casuarina leaves (green needles) were also investigated but the tan content found was too low to be of any use.

In the case of both the root and the bark, the tannin content is quite appreciable with a rather high T/N.T. ratio. The pH values of the tanliquors prepared from the root and bark of the Casuarina trees are 4.65 and 4.8 respectively which compare favourably with those of other tan liquors of comparable strength prepared from the common South Indian tan materials like Avaram and Konnam both of which have a pH of 4.7. The corresponding value for Wattle was found to be 4.6.

Casuarina tannin especially that obtained from the bark contains very considerable amount of salts of weak acids. The acid content also is appreciable but the presence of appreciable amount of buffer salts gives a resultant pH of 4.7 only. The nature of the titration curve shows a distinct flatness between pH 3 and 2. Even at pH 2.0 it appears that some salts of weak acids still remain to be back titrated.



Leaching efficiency at Optimum Temperature was determined by extracting 100 grams of the material (Bark or Root as the case may be) with 400 ccs. of distilled water at the pre-determined temperature. The figures thus obtained for the bark and the root are 88 and 82 respectively.

It was found that at 60°C the maximum amount of tans were extracted both from the root and the bark the values being 12.3 gms. and 8.83 gms. respectively per 100 gms. of materials taken. Increase of temp. to 70°C was found to lower the per cent of tannins extracted, the corresponding figures for the above values being 11.3 and 9.29 respectively. Moreover at the higher temperature the non tannins from the bark shows an appreciable increase. Hence 60°C appears to be the Optimum Temperature of extraction for both these ingredients of Casuarina tree.

Comparative study of the penetrating capacity of the liquors through the pelt show that the liquor from the root penetrate more easily than that obtained from the bark. Both the liquors were found to impart a rather dark shade to the leather produced. However the Casuarina tannin is much better in this respect than many of the mangroves. Preliminary work shows that this tannin from the Casuarina tree is amenable to chemical treatment for the improvement in the colour without adversely affecting its tanning properties. Further work in this direction is in progress.

Besides being used as fuel Casuarina trees have many other uses. It is used for building posts, electrical poles etc and a decoction prepared from it is used as a medicine for Beri Beri. For these purposes, extensive plantations of Casuarina are being raised, and these should prove to be a regular source for the supply of tanning material at considerably low cost to the tanning industry especially in the rural areas.

Author's thanks are due to the Asst. Director-in-charge for permission to publish the paper.

Director's Laboratory,  
8—12—1956.

S. VENKATARAMAN,  
S. K. BARAT

#### REFERENCE

1. Wealth of India, Raw Materials, Vol. II, Page 101.

## RESEARCH BEARS FRUIT

Practical Demonstration No. 1

### MANUFACTURE OF CHROME RETAN LEATHERS

A. GANESAN & Y. NAYUDAMMA

#### Note :

This process has been specially worked out for loose textured hides of poor substance from naturally dead animals. Leathers made by this process having a thickness of 2 to 2.2 mm. are being regularly used as uppers in slippers and chappals without lining. When somewhat tight textured hides are to be processed, this method has to be modified the details of which will be published elsewhere. This method has been worked out to cut down costs to the maximum. The process is detailed below :

*Raw material :* Raw material for the type of retan leather described herein is wet salted cowhides of 25 to 26 lbs. average weight. Hides selected are usually rejections and double rejections unsuitable for chrome upper. Most of the hides have hair slips, serious grain damages and loose texture.

*Soaking :* The selected hides are trimmed to remove the cheek and leg pieces and weighed. This weight is recorded as salted stock weight and the percentages mentioned below are on this figure.

Clean water at 400% on the weight of hides is put in a soak pit and the hides are entered. The hides are trampled for 15 minutes and the bath is drained. An adjacent pit is filled with equal quantity of water to which 20% salt and 0.4% of caustic soda flakes are added. The bath is now well stirred, tested and found to be alkaline to phenolphthalein. Hides are then entered one by one into this pit and left overnight.

*Liming :* Next day morning, the hides are taken out and cut into sides. They are then transferred to another pit containing the same quantity of fresh water. Trampling is done for 15 minutes. The hides are then taken out and allowed to drain.

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The unhairing paint is prepared in a wooden tub as per the following recipe :

Shell lime powder 20%  
Sodium sulfite 60 to 62% strength—1.5%  
Water 30%

Sides are dipped one by one in this paint and piled flesh side up in an empty lime pit. The pile is then covered well and left overnight. Next day morning they are taken out and loaded in a washing drum (r.p.m. 14 to 16). Water is filled up to the axil. The drum is put in motion with the lattice door on, and fresh water is continuously run in through a rubber hose. Washing is done for 10 minutes. The bath is then drained. The drum is filled upto the axil as before, run for 10 minutes and drained again. Next water is filled upto the axil, run for 5 minutes and drained. The goods are now taken out and they are now clean and free from hairs, scud etc. No unhairing is necessary. Sides are now fleshed by machine and the pelt weight is taken.

(Another method of liming is given below for hides of tighter texture.

300% water is put in a lime pit. 5% shell lime and 0.75% sodium sulfide, (60 to 62% strength) are added. Hides are entered and left overnight. Next day, handling is done as usual and on the third day hides are unhaired, fleshed, weighed and the pelt weight recorded.)

Coming back to the first process, the fleshed hides after weighing are put in a paddle containing clean cold water at 400% on pelt weight. The paddle is run for 10 minutes and the bath is drained.

*Note :* All percentages given below are on the pelt weight.

*Deliming :* The paddle is again filled with the same quantity of water, run for 30 minutes and drained. Refilling is done as before and 1% ammonium sulfate is added. The paddle is run for 20 minutes and rested for an hour, run for 10 mts. and again rested for half an hour. 1% sulphuric acid diluted 10 times is added. Run the paddle for half an hour and allow it to rest for some time. The paddle is again run for 5 minutes before running overnight. The bath should be just alkaline to phenolphthalein.

Next day morning, the paddle is run for half an hour. Sides are now transferred to a drum of 4 to 5 r.p.m., filled with water

upto the axil. Washing is done for 15 minutes and the bath drained. Another wash is given for 10 minutes and the bath is drained.

*Note :* No hand scudding is given at this stage also.

*Pickling :* 80% water is put in a wooden tub, 4% salt is added and dissolved. This solution is added to the drum and run for 5 minutes. 3% of concentrated sulphuric acid, 66% B.E. is diluted with 10% water, cooled and added. The drum is run for another 15 minutes. Again 3% sulphuric acid, diluted with 10% water, is cooled and added. The drum is run for 15 minutes after which 1% sodium formate is added as dry powder. Continue the drumming for another 30 minutes.

*Chrome tanning :* Chrome liquor for tanning is made up as below :

7% of solid chrome extract powder (made by Buckingham & Carnatic Co., Madras) is put in a tub and covered with 20% water. Stir occasionally. Leave overnight and by next day a clear solution is obtained. Add the entire chrome liquor to the pickle bath in one feed. Chrome liquor may also be prepared as per the following recipe.

Bichromate 100 lbs.  
Sulphuric acid 66° B.E. 100 lbs.  
Molasses 40 lbs.

The liquor may be made upto 500 lbs, total so that 20 lbs, of this chrome liquor will contain one pound bichromate. That amount of chrome liquor which is equivalent to 3.5% bichromate on pelt weight is added to the drum. The hides are run for three hours, piled outside and left overnight. Next morning, 4 oz.% of sodium bicarbonate is added directly to the drum, mixed well and the hides are put in and run for  $\frac{3}{4}$  of an hour. The pH of the liquor should be 4. Hides are piled.

*Sammying and splitting :* The tanned sides are sammed, split to 2.25 mm., weighed and the split weight is noted. The split sides are run in the exhaust chrome liquor for 45 mts. and piled on horse and left overnight.

*Neutralising and washing :*

*Note :* All percentages below are on the split weight.

Enter the stock in a drum of 4 to 5 R.P.M. containing 200% cold water. Wash for 10 minutes and drain. Give another wash for 10 minutes, drain and refloat with 200% water. 0.5% sodium bicarbonate is added in 4 instalments at 15 minutes interval. The drum is run for 20 minutes after the last addition of soda. A cut piece is taken from the thickest part of the hide. A drop of Bromocresol green is applied to the cut edge. When only a thin yellow streak is seen at the middle of the cut edge, the bath is drained and the stock washed for 15 minutes in 20% water. Refloat with 60% cold water.

*Fatliquoring*: Add the fatliquor made up as below:

Sulpholine A: 4%  
Pungam oil: 1%  
Emulsified with Water: 15%

This fatliquor is added in one feed into the drum and run for 20 minutes. The bath is drained. Refloat with 100% water.

*Retanning*: Add 5% solid myrab extract, previously dissolved in the minimum quantity of water and adjusted to pH 7.0 by careful addition of caustic soda.

The drum is run for 45 minutes and drained. Now, the exhaust vegetable tanliquor from the previous lot equal to 100% on the split weight of leather is put in. The goods are run for 30 minutes in the weak liquor and drained.

*Retanning*: Put 60% water in the drum. The retanning extract liquor made up as below is added.

Preparation of stock solution:

Put in a vat 15% solid myrab extract and 10% solid wattle extract and cover with the minimum quantity of water. Pass steam into it and dissolve completely. The total quantity of solid extract taken is 25% on the split weight. After complete dissolution, enough caustic soda is added to bring the pH of the liquor to 5.5. The liquor is adjusted to 100°Bk by adding sufficient water. The stock solution is ready for use.

*Note*: The total quantity of extract used and the blend mentioned may be modified to suit different types of hides. It is preferable to do an assortment of the blue stock before the retanning. Mellow blends should be used for hides of tight

texture. Some of the formulations that have proved good are given below:

Formula A: 5% totannin.  
10% wattle  
10% myrab.

Total 25%

Totannin is dissolved separately and added into the drum, run for ½ hour, then the latter two are added in three instalments at ½ hour intervals after having adjusted to pH 5.5

Formula B: Where greater filling is desired:

Totannin 5%  
Wattle 15%  
Myrab 10%

Total: 30%

Formula C: Totannin 5%  
Wattle 12%  
Myrab 8%

Formula D: Cutch extract No. 2 18%  
Myrab extract 7%

Larger quantities of extract for greater filling but more fat also must be put in. The cost of operation therefore further increases.

Whatever blend is used, the drum is run for 3 hours and the operations may be considered over when the looser portions of the hides are well filled up and the tighter portions show about ¼ to 1/3 penetration from the flesh side. Too much tightening up of the already tight area is undesirable.

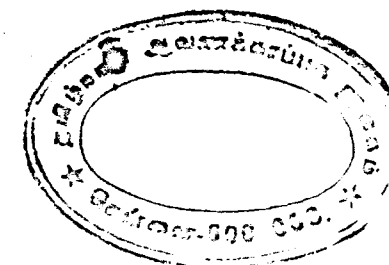
The exhaust tan liquor is run into vats for use in the next lot.

Cold water is run into the drum upto the axle, run for 5 minutes and drained. The hides are pulled out, rinsed and piled.

*Oiling, Sammying, Setting and Drying*: The retanned sides are struck out and the grain oiled up with the following mixture:

2% sulpholine A  
½% tallow  
1% Pungam oil  
1% spindle oil

(All percentages on the split weight).



Application of the oil mixture is made on the grain. More oil is applied on the tighter portions and less on the looser ones. After oiling, sides are hooked up, sammied, set out by machine twice and then by hand. The drying is completed in the lofts as usual and then the sides are piled for 2 days.

*Conditioning and Staking*: Dried sides are sawdusted as usual and staked carefully. Staking should not be done as for regular chrome side upper. The staking machine should be so adjusted that the sides are not pulled and peeled sharply. The tighter portions may be staked at higher pressure.

*Levelling*: Staked sides be levelled up to a substance of 2.0 to 2.2 mm. either by deep buffing or shaving where necessary. The sides are now trimmed.

*Buffing*: Buff the flesh side with No. 100 emery paper. The grain side is buffed deep with old 180 or 240 followed by 400 paper.

*Staining*: The grain and flesh sides are stained with 2 oz. of basic dye per gallon of solution. The stain solution is sprayed. The composition of the stain solution is given below:

**Black:**

- 2 oz. of Methic Leather Black D (I.C.I.).
- 4 oz. Glycerin.
- 1 oz. Triton x 100 (Amrital & Co.)
- Water to 1 gallon.

**Brown:**

- 2 oz. Bismark Brown RLNS
- 4 oz. glycerin.
- 1 oz. Triton x 100 (Amrital & Co.).

*Finishing*: Dye coat: A dye coat is prepared as below:

- 2 oz. Chlorazol Black E240
- 1 oz. Nigrosine
- 1 oz. Hematin
- $\frac{1}{2}$  oz. of Ammonia
- Water to 1 gallon.

This dye coat is applied by brush on the grain side. Air off.

*Pigment Coat*: Pigment coat is prepared as follows:

- 4 oz. of Black pigment paste.
- 2 oz. Chlorazol Black E 240 (I.C.I)
- 1 oz. Hematin dissolved with a few drops of ammonia.

- 1 oz. Nigrosine.
- 4 oz. Casein 10% solution (Prepared with borax as usual).
- 6 oz. Bedacryl 100A. (I.C.I.).
- 8 oz. of wax emulsion.
- 4 oz. of formalin.
- Water to make 1 gallon.

The pigment coat is applied twice by hand, air off, dry and spray the same solution diluting it with 50% of its weight with water. When greater coverage and luster are desired, spray the 5% wax emulsion mixed with 2½% casein solution (1:1) as a middle coat followed by a spray of the diluted season.

*Top Spray top coat* made as below solution:

(Borax dissolved) casein 2½% 100 parts

Commercial formalin diluted 1:1 with water 75 parts.

Spray twice. Then measure the sides, smooth plate them at 130°F, assort and pack.

*Brown*: The dye coat is matched to final shade, Dye solution being 2 oz. per gallon. Apply finish made as below:

- 4 oz. of light brown pigment paste
- 4 oz. of tan pigment paste
- 6 oz. Bedacryl 188A
- 4 oz. casein 10% solution
- 4 oz. of ammonia
- 4 oz. of formalin and 12 oz., of wax emulsion as mentioned before.
- 200 cc. 2% solution (naph. leather brown) water to make 1 gallon.

Apply the pigment coat twice by hand. Dry, spray the same diluting with 50% of its weight with water. For greater coverage and luster, spray the 5% wax emulsion mixed with 2½% casein solution (1:1) as a middle coat. Spray the final pigment coat with the diluted season.

*Top*: Spray top coat made as below:

Borax dissolved casein 2.5% strength 100 pts.  
Comm. formalin diluted with 1:1 water 75 pts.

This may be sprayed twice. Then measure the sides, smoothplate them 130°F, assort and pack.

## TECHNICAL SEMINAR \*

### NEW TANNING MATERIALS

M. K. UDAYA VARMA

Though India abounds in a variety of vegetable tanstuffs, only a few of them like Babul, Avaram, Myrobalans etc., are used in commercial tanning. Tanning materials worth about 80 lakhs of rupees are annually imported. So investigations to find out new materials were undertaken and these have resulted in the finding of two new materials, viz., *Peltophorum ferrugineum* and *Pithecolobium dulce*. These materials have been found to grow well in Madras, Kerala and other parts of India. They require no particular soil, altitude or climatic conditions. Moreover, they have no other commercial value than as fuel. The tannin content of these barks are 20.3 and 33.9% respectively.

E.I. tanning experiments have shown that *Peltophorum* produces a light coloured full and strong leather of desirable feel very similar to the E.I. kips. A soft, tight grained leather which is slightly dark was produced by *Pithecolobium*. To effect further improvements in tanning characteristics, acid-salt adjustments of these tan liquors were carried out. For *peltophorum* acid-salt adjustment does not appear to be advantageous for E. I. kip tannage but for *Pithecolobium*, the addition of sodium sulphate in small quantities is beneficial. Blending of *Peltophorum* bark with Myrob (6:1) and Konnam (3:4) gives very good results. *Pithecolobium dulce* blended with myrob (6.5:1) and with Konnam (5:8) also produces very good E.I. leather.

These barks are also found to be useful for sole leather tannage. Other materials which are being investigated are the barks of *Thespesia Populnea* (tans 8.8%) and *Odina Wodier* (tans 11.3%) and leaves of *Cassia Marginata*, Cashew nut and *Peltophorum*.

---

\* Summary of Technical Seminar held on 30-10-'56.

## CLASSIFIED ABSTRACTS

### RAW MATERIALS

STUDIES OF THE NITROGENOUS COMPONENTS OF HIDES AND SKINS. I. THE INFLUENCE OF INITIAL PROCESSING ON FRESHLY FLAYED CATTLE HIDES. F. L. DeBeukelaer and E. P. Marbach. *J.A.L.C.A.* 51, 11, 592, (1956). A method for preparing reproducible hide samples in a highly subdivided state is described. The procedure employed in separating the nitrogenous components of hides into five fractions and in quantitative assay thereof is given for both the fresh and the cured state. The chief difference found between a brine-cured and a green-salted product is that the latter contains approximately six times more non-protein nitrogen material than does the brined sample.

### TANNING

TANNING STUDIES WITH AN EPOXY RESINS. PRELIMINARY EVALUATION OF THE LEATHER. I. D. Clarke, E. H. Harris, Jr., & E. M. Filachione. *J.A.L.C.A.* 51, 11, 574 (1956). Steer hide blocks, split to 8 ounces, were tanned with an epoxy resin, Epon 562, and changes in the crust-dry leather relative to acetone-dehydrated stock were noted. The weight and thickness gain and the loss in area were comparable to those noted with chrome-tanned stock. Tanning with the epoxy resin resulted in lower stretch and greater stiffness in flexure than did chrome or vegetable tanning. The epoxy resin tannage also resulted in a greater loss of strength compared with chrome and vegetable tannage. The leather obtained upon tanning with Epon 562 showed reversible shrinkage (Ts85°C.). The properties discussed above were not significantly altered upon boiling this leather in water for one minute or upon retannage with chrome or vegetable tannin.

CORDOVAN LEATHER FROM PIGSKIN. W. Frankford. *Das Leder*, 7, 109-110 (1956). *Via. J.A.L.C.A.* 51, 11, 627, (1956). The rear back part of skins of old hogs, if tanned by the process used for horse shells, will make shoe upper leather similar to shell cordovan. A comment by A. Kuntzel and T. Stirtz (with photomicrographs) points out that pigskin does not have a structure similar to that of the shell area of horsehides, although this does not mean a cordovan leather cannot be made from pigskins.

THE ACTION OF SULFITING ON THE SOLUBILITY BEHAVIOUR OF VEGETABLE TANNINS. D. G. Roux. *Das Leder*, 7, 111-12 (1956). *Via. J.A.L.C.A.* 51, 11, 625 (1956). Chromatographic studies indicate sulfitated components of an extract do not emulsify insolubles, because these have already been made soluble by sulfiting. Sulfiting decreases the affinity of tanning for cellulose and collagen. There is at present absolutely no proof that sulfiting decreases particle size.

NEW PROCESS FOR QUICK LOW-COST TANNING. *Aust. Lea. J.* 59, 9, 116, (1957). A new process for rapid and economical tanning of sheepskins and other skins of all descriptions has been worked out by an industrial Research chemist and is being developed on a commercial scale in association with one of the largest tanneries in New Zealand.

The process is the result of some years of experimentation and has been demonstrated before leading tanners, who have declared that the leather produced is of excellent quality.

Skins tanned by this method are given preliminary treatment by immersion in a bath containing one or more substances, at atmospheric temperature. After a short time the skins are transferred to a bath of tannage, such as chrome or wattlebark solution or other similar astringent, which immediately enters into the fibrous tissues of the skins. The total time required to complete the immersions in the two solutions whether skins are furred or without fur is from 45 to 60 minutes. When dressed with a non-formalin material, the resulting leather is of attractive whiteness and is claimed to have long lasting qualities.

An important feature of the preliminary treatment is that it greatly reduces the time and labour necessary to produce first grade leather at low cost. The process, which is protected by world patent rights, is inexpensive and requires no special plant. No deterioration in the leather is anticipated with the passing of time as none of the substances used is present in the finished leather, or is capable of injuring it.

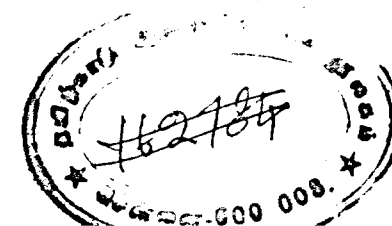
All leathers produced and manufactured under the process in the Dominion will be known as "liberty leathers".

A REVIEW OF FUR-SKIN DRESSING, ITS HISTORY AND METHODS. *H. Kaplan British Fur Trade*, 418, 419, 422, 425, 478, 480 (Nov. and Dec. 1955. *Via. J. Soc. Dyers and Col.* 72, 10 508, (1956). Following a brief outline of the history of fur dressing it is stated that the first of the modern fur garments, the black fur-seal jacket, appeared only about 1842 and 1932 Leipzig was the world centre of fur dressing but now each centre of the fur trade—London, New York, Frankfurt, Paris and Milan—has its own group of fur dressers. There is great variation in the processing of fur skins but generally it follows the lines of soaking in sterile brine, fleshing, pickling, and greasing. The most common pickling agents are sulphuric acid, lactic acid, alum and common salt and occasionally chrome or formaldehyde. Pickling is done either by immersion in the acid or salt solution or by brushing a concentrated solution on to the pelt. Alum-dressed furs are usually less stretchy than sulphuric-acid-pickled skins, more resistant to wetting and heavier. For special purposes, particularly Persian lambs, a fermentation or "meal" pickle is used. Bran, oats or similar cereal is fermented and the sour liquor applied by hand or by steeping. The liquor contains small quantities of organic acids but it is more likely that removal of mucoids by the proteolytic enzymes present is the real cause of the softness and lightness of the resultant leather. Chrome and semi-chrome are used on sheep, lambs and other skins which have to be hot processed, e.g., ironed, or dyed in hot liquors. Chrome yields a thicker and heavier pelt than acid dressing, tints the fur or wool pale green and

gives risk of damage on subsequent bleaching or dyeing with use of peroxide. Formaldehyde gives a soft and light pelt but insufficiently stretching and although it does not affect the colour of the fur, the large amount taken up complicates subsequent dyeing. It is used to a limited extent in combination with acid or alum pickle. Vegetable tans are rarely used, they yield a thick heavy pelt, the fur is invariably tinted and the skins are very sensitive to alkali. After pickling the skins are hydroextracted, stretched and greased to impart softness, pliability and resistance to tearing. Fatliquoring is not normally practised as it necessitates further treatment to remove the grease absorbed by the fur. There are two main methods of greasing, "stove" and "kicker". The stove method is suitable for thin-pelted and fairly open-grained skins, e.g., lambs, rabbits, foxes, sables. Sulphonated fish or animal oils together with paraffinic mineral oils are swabbed on to the pelt which is then stove dried at 90-120°F. under controlled R.H. In the kicker method sod oil, unsulphonated fish and animals oil, mineral oil and wool grease in combination are worked into the skin by wooden feet moving horizontally inside a wooden casing. It is only a mechanical adaptation of treading the oil into the skins by a man's feet. The skins are then drummed with sawdust to remove excess grease before stretching, handling or staking. Finally various mechanical treatments—shearing, ironing, beating with canes, combing or carding—are used to enhance the appearance of the furs. During the last two decades processing of woolled sheepskins has become a separate industry which uses various modifications of treatment with formaldehyde followed hot ironing to produce the so called Beaver Lamb. The skins are soaked and fleshed and the wool scoured and deburred. Pickling and tanning follow, the best being a semi-chrome with a  $\text{Cr}_2\text{O}_3$  content of about 1.5%. Oiling, drying, drum cleaning and staking follow after which the skins are examined for suitability for Beaver Lamb, the criteria being fine dense wool, soundness of grain, and freedom from ribbiness. The rejected skins are used for slipper linings, collars, rugs, etc. Preparation for dyeing Beaver Lamb involves considerable mechanical and chemical treatments to produce an evenly shorn surface having permanent gloss and free flowing fur.

## PROCESSES AFTER TANNING

NITRO CELLULOSE LACQUERS. *J. Sommer. Aust. Lea. Tr. Rev.* 52, 12, 15, (1956). Though the so-called plastic finishes containing plastic polymer dispersions have become popular in recent times, nitro cellulose lacquers are still used in the leather industry to a very large extent. Nitro cellulose is produced by treating wood cellulose with nitric and sulphuric acids and is supplied in the form of white fibres, mass or powder. A certain degree of nitration i.e., to the extent of 10.5-12.2% nitrogen is required for leather lacquers. Since nitro cellulose, when used alone in solvent, forms a brittle film, it is necessary to incorporate some suitable plasticisers which soften the film and form itself a solvent for nitro cellulose. The elasticity of the film migration of the plasticiser from the film into the leather, solubility and light stability are important factors to be considered in the selection of suitable plasticisers. Diamyl phthalate, Dioctyl phthalate, citrates, andipates and phosphates are some of the common plasticisers.



The solvent mixture should produce a lacquer of maximum concentration of solids, should be of low viscosity and evaporate as soon as the coating has levelled out, the rate of evaporation being not too rapid.

A diluent is a liquid miscible with solvents in all proportions but not itself a solvent for nitro cellulose. Mixtures of solvents and diluents are known as thinners. During the addition of diluents, care should be taken to see that the lacquer components do not precipitate due to the change in composition during evaporation. This effect which produces a cloudy film is known as "Cotton Blush". Diluents are now ever useful in bringing about a homogeneous solution of nitro cellulose lacquers.

V.V.S.

**COVERING POWER OF PIGMENTS USED IN LEATHER FINISHING.** E. Belavsky and T. Termignoni. *Rev. Quim. Industr. Rio de Janeiro*, 24, 21, (1955); *J. Appl. Chem. Abs.*, ii, 824, (1955); *J. Soc. Lea. Trades Chem.* 40, 244 (July 1956); For good finishes, particle size of the pigment must be air-and light-fast. Covering power depends on the comparative refractive indices of pigment and medium. Three general bases are used for leather finishing—casein, cellulose nitrate, and polyacrylic or polyvinyl resins. Tests were made using a number combinations of medium and pigment. Titanium oxide, with its high refractive index (2.30-2.46) has high covering power in all media, especially synthetic resins, and may be cheapened by mixing with barium sulphate. A table gives pigments and media for leather finishes of various colours.

**THE IDENTIFICATION OF VAT DYES.** D. A. Derrett-Smith and J. Gray. *J. Soc. Dyers Col.*, 1956, 72, No. 5, pp. 211-227. *Via. J. Text. Inst.* 47, 10, A489, (1956). The tables published in 1940 by Derrett-Smith and Bradley<sup>1</sup> and in 1949 by Derrett-Smith and Gee<sup>2</sup> have been brought up to date to include all the British, German, and Swiss vat and solubilized vat dyes which have appeared on the British market since 1940. Dyes which were included in the original tables but have since been made by other firms are included under their new names. In addition, it is shown that certain vat dyes behave differently when treated with sodium hydrosulphite and sodium hydroxide as compared with sodium hydrosulphite and sodium carbonate. (1. *J. Text. Inst.*, 1940, 31, A407 and 2.1948, 39, A253).

### GENERAL

**THE MECHANICS OF LEATHER.** Elcana Peterson. *Leather & Shoes*, 132, 21, 16, (1956). The various problems that a tanner faces during the various operations of leather manufacture have been discussed. The cutting of hides into sides, if not done through the hair line, will show undesirable results in the subsequent operations. The sides start to roll or curve along the back and are liable to be damaged in beaming and unhairing operations. By the proper choice of the cylinder pitch and rubber roll density of the fleshing machine, the lime fleshing may be avoided and soak fleshing done. The wire edges should be removed from the freshly ground cylinder of the machine, thus avoiding chatter. Excessive plumping of the hides or too much pinch roll pressure will cause tiny grain cracks. The nicks in brass cylinder blades of the un-

hairing machine cause grain damages to the leather by scratches. Drums with the same size, pins and shelves running at the same rpm. are recommended with a view to get uniform results. Plastic door for drums will be easy for handling due to their lightness. The troublesome chatter during splitting of vegetable tanned leather may be overcome by using heavier gauge blades. For flat grain, setting out at a higher roll pressure and angling the side when setting, is recommended. Flatter grain, less trimming and more products results from paste drying than from toggling and high air velocity gives uniform drying. For buffing the grain, an oscillating machine will give better results than a non-oscillating one.

V. V. S.

**PREVENTION OF MICROBIOLOGICAL DETERIORATION OF LEATHER.** Sverre Dahl. *J.A.L.C.A.* 51, 3, 103, (1959). The prevention of microbiological deterioration of leather starts with the freshly flayed hide. Any destruction of collagen by bacteria prior to tanning cannot be compensated for by the tanner's skill and experience, and will result in inferior leather. The methods used for protection of the hide prior to and during tanning operations are briefly discussed. Tanning makes collagen resistant to micro-organisms, but leather adjuncts, such as oils and greases, are excellent nutrients for molds, especially *Aspergillus niger*. Due to the removal of leather adjuncts by such molds, the leather becomes stiff and brittle, and its usefulness is impaired. Fungicides are now being used to prevent this deterioration. Methods used for the evaluation of fungicides for this purpose, and the types of compounds found to be most effective, are discussed.

**STABILIZATION OF EDIBLE ANIMAL FATS DURING RENDERING.** Rex J. Sims and Lee Hilfman. *J.A.O.C.S.* 33, 9, 381, (1956). Studies have shown that lard and edible beef fats can be stabilized effectively with phenolic antioxidants during pressure steam rendering. Best results were obtained for a given stabilizer level with the individual phenolics butylated hydroxyanisole and butylated hydroxytoluene. Poorer results were obtained with the mixtures in propylene glycol.

**EPOXY FATTY ACID ESTER PLASTICIZERS. PREPARATION AND PROPERTIES.** Frank P. Greenspan and Ralph J. Gall. *J.A.O.C.S.*, 33, 9, 391, (1956). The preparation of epoxy fatty acid ester plasticizers has been reviewed. These plasticizers can be prepared by epoxidation reactions, utilizing a preformed peracid or an *in-situ* technique. A new *in-situ* epoxidation process, utilizing hydrogen peroxide and acetic acid in the presence of strong acid catalyst, has been described. Excellent conversions to epoxide have been achieved with a series of mono-unsaturated and poly-unsaturated esters.

Epoxy fatty acid esters are excellent plasticizers for vinyl resins. Their performance in a series of additional epoxy plasticisers of vegetable and marine origin is described. Novel epoxy plasticizers based upon mixed acetylated mono—and di-glyceride have been prepared and are found to have excellent plasticizer performance.

**THE ADSORPTION OF ALCOHOLS AND PHENOLS FROM NON-POLAR SOLVENTS ON TO ALUMINA.** D. J. Crisp. *J. of Col. Sci.* 11, 4 & 5 356, (1956).

1. The isotherms for adsorption from benzene solution on to dry alumina were measured by means of the surface balance for a number of surface-active materials, chiefly alcohols. The isotherms were of Langmuirian form, described by  $q_c(1 - \theta) = K$ , where  $K$  is the Langmuir adsorption coefficient.

2. Competitive adsorption was followed between two alcohols, and between an alcohol and a phenol. The two adsorbates followed the Langmuirian equation independently, and the coefficient of adsorption of one could be deduced from the coefficient of the other.

3. When one of the competing substances was water, competitive adsorption did not appear to follow the Langmuir isotherm, since the water did not desorb normally.

4. The isosteric or differential heats of adsorption of several surface-active substances were measured from the temperature dependence of the Langmuir adsorption coefficient. The calorimetric or integral heats were also measured and were somewhat higher than the differential heats.

5. The heats and free energies of adsorption were in all cases independent of the length of the hydrocarbon chain. The free energy and probably also the heat of adsorption in the series alcohol, phenol, fatty acid increased as the hydroxyl group became more acidic.

6. The molecules are believed to be adsorbed on fixed sites of approximately uniform energy. At low concentration of adsorbate its nonpolar region remains dissolved in the solvent and is not affected by adsorption. The presence of solvent minimizes lateral forces and this allows the Langmuirian relationship to hold good over a wide range of surface coverage.

7. The Traube rule, if applied to energies of adsorption, is probably generally valid for adsorption on solid surfaces. The so-called exceptions are thought to be due to the smaller surface area often available to larger molecules rather than to any decrease in their molar energy of adsorption.

8. The adsorption of polar substances from nonaqueous solutions appears to be little influenced by the hydrocarbon chain with silica as the adsorbent just as with alumina. On the other hand, the energy of adsorption of organic molecules from aqueous solution on to charcoal increases with increasing length of the hydrocarbon chain.

**ACTIVITY OF TRYPSIN-LIPID COMPLEXES AT OIL/WATER INTERFACES.** M. J. Fraser and J. H. Schulman. *J. of Col. Sci.* **11**, 4 and 5, 451, (1956). Adsorption of trypsin at lipid-stabilized oil/water interfaces has been studied as a function of the nature of the interface. The adsorption of the enzyme, with corresponding changes in the activity expressed, is found to be related to the charge and nature of the lipid polar groups at the interface and, to the charge and nature of the polar groups of the protein. Interactions between enzyme and lipid at

the interface are paralleled in bulk with soluble lipid homologs. The loss in activity of the enzyme at the interfaces studied is thought to be due to a general structural unfolding of the molecule. Provided that the unfolding process has not gone too far, desorption of the surface enzyme can lead to partial recovery of activity.

Some of the problems involved in the study of the effect of changes in the general structure of the protein on the enzymatic activity by the present methods are discussed. It is concluded that a determination of whether or not these partially "denatured" enzymes can work at lower efficiency necessitates careful investigation of the kinetic and thermodynamic properties of the adsorbed, partially unfolded enzyme.

**ESTERS IN HUMAN HAIR FAT.** N. Nicolaidis and Roscoe C. Foster Jr. *J.A.O.C.S.* **33**, 9, 404, (1956). A study was made of the hair fat composition of human adults with special reference to its ester content. Waxes, triglycerides, and a mixture of mono—and di-glycerides were isolated and characterized. Indirect evidence is presented that the free acids of hair fat are derived from lipolysis of triglycerides. Some preferential esterification of some kinds of fatty acids as glycerides and others as waxes was observed. No significant differences could be observed in the analysis of the hair fat of adult males compared with that of adult females of the same age group.

**CONTROL OF SLUDGE VOLUMES FOLLOWING LIME NEUTRALIZATION OF ACID WASTES.** S. D. Faust, H. E. Orford and W. A. Parsons. *Sew. & Ind. Wastes*, **28**, 7, 872, (1956). A series of laboratory experiments was conducted to examine sludge return processes for control of sludge volumes resulting from the high-calcium and dolomitic lime neutralization of waste sulfuric acid solutions.

Three processes are presented as follows:

1. Addition of native gypsum powder.
2. Return of a sludge initially seeded with gypsum.
3. Return of unseeded sludge.

## TESTING

**EVALUATION OF METHODS CURRENTLY USED TO DETERMINE B.O.D., C.O.D. AND ODOR FOR INDUSTRIAL WASTES.** M. B. Ittinger. *Sew. & Ind. Wastes*, **28**, 9, 1116, (1956).

1. The use of odor tests for evaluation of industrial effluents in terms of possible harmful effects on surface waters has been discussed, and the general functional requirements of adequate test procedures considered.

2. It is sometimes difficult to measure the biologically oxidizable organic material in an industrial waste because of the difficulty of securing effective "seed" for laboratory use.

3. Chemical oxygen demand tests such as the Moore procedure (7) using silver catalyst usually indicate higher values than the B.O.D. test on an industrial waste. The C.O.D. test gives a relatively rapid measure-

ment, and usually determines most of the oxygen which can be used in completely oxidizing carbon compounds present.

4. Joint use of B.O.D. and C.O.D. tests on industrial waste problems, frequently is highly advantageous. In many cases analysis of the cause of differences between the two values can be very informative and may develop significant information.

**LABORATORY AND FIELD EXPOSURE STUDIES OF LEATHER FUNGICIDES.** *Sverre Dahl and Arthur M. Kaplan. J.A.L.C.A. 51, 3, 118, (1956).* The effectiveness of seven experimental leather fungicides that were previously evaluated in laboratory tests has been studied under field conditions together with 4-nitrophenol as the comparison standard. In addition to 4-nitrophenol, it was found that 2-chloro-4-nitrophenol, 4-thiocyanophenol, and bis (4-nitrophenyl) carbonate prevent mildew growth of leathers under tropical jungle conditions at concentrations no higher than 0.60 per cent and are adequately stable under severe weathering conditions. N-(trichloromethylthio) tetrahydrophthalimide and tetrachlorohydroquinone inhibited mildew growth at 0.60 per cent concentration in some cases, but are not dependable leather fungicides. 2-Phenyl-phenol and 4-chloro-m-xenol are not effective leather fungicides even at concentration well over one per cent.

**QUANTITATIVE ANALYSIS IN THE 2-REGION APPLIED TO SYNTHETIC POLYMERS.** *R. G. J. Miller and H. A. Willis. J. Appl. Chem. 6, 9, 385, (1956).* The application of short-wave (below 2) spectroscopy in the examination and analysis of synthetic polymers is described with special reference to molecular weight determination by end-group estimation, determination of monomer in polymers, and analysis of copolymers.

**USE OF THE THIOHYDANTOIN METHOD FOR THE DETERMINATION OF THE TERMINAL CARBOXYL AMINO ACIDS OF COLLAGEN.** *C. Deasy. J.A.L.C.A. 51, 11, 584, (1956).* The thiohydantoin method for the determination of terminal carboxy amino acids was applied to collagen. Glycine, alanine, and leucine (or isoleucine) were found and may be regarded as the terminal carboxyl amino acids of collagen (subject to the limitations of the method).

**NEWLY DEVELOPED AND IMPROVED TESTING MACHINES FOR THE LEATHER AND PLASTIC INDUSTRIES.** *H. Rodenhauser. Das Leder, 7, 82-84 (1956). Via. J.A.L.C.A. 51, 11, 624, (1956).* A description with illustrations is given of 3 testers: (1) a folding endurance tester, probably similar to the MIT paper tester (parts on the figure are not lettered, although lettering is used in the text); (2) the Bally Flexometer for determining folding resistance; and (3) an abrasion-resistance tester in which the specimen is rotated while moving horizontally across a rotating cylinder covered with emery.

**ADHESION TEST FOR LEATHER FINISHES.** *W. Schweisheimer. Aust. Lea. J. 59, 9, 111, (1957).* A test has been developed by Maynard B. Neher, Batelle Memorial Institute, for measuring the adhesion of finishes to leather which gives adhesion results practically independent of

other finish properties such as elasticity and flexibility. In this new test a copper strip is bonded to the leather finish by means of a heat-activated phenolic bonding film under moderate pressure. The force required to remove the copper strip, bonding film and finish vertically from the leather surface is determined by conventional tensile strength apparatus.

The bonding film adhesion test has been applied to a variety of leathers under differing conditions. In general, the finishes on kid leathers show very low adhesion values, cowhide shoe upper leathers show intermediate values, and upholstery leathers show high values. Within prescribed limits variation of bonding temperature, pressure and time do not significantly affect the adhesion values obtained.

Several new adhesives have been found recently which adhere to a wider range of finishes, according to Mr. Neher. A mixture of Versamids 100 and 950 (General Mills) works well on nearly all finishes except vinyls. For vinyl finishes, a vinyl chloride vinyl acetate polymer VAGH (bakelite) appears to give good results.

A statistical analysis was made by Mr. Neher on one set of experiments. The experimental error (standard deviation) was found to be 0.39 lb./in. based on 160 determinations. Therefore, 95% confidence limits are  $X \pm 0.78$  where X is the average of no determination. This test should be useful in research on leather finishing, as well as in development and control of tannery processes.

## PATENTS

**NEW FRENCH PATENT FOR RAPID TANNING.** It was reported at a recent B.L.M.R.A. meeting that Secotan Incorporated had brought out a patent for solvent chrome tannage under pressure (French Pat. 1,093,089).

According to the specification, skins are laid flat on a porous material (e.g., wool felt 6.3 mm. thick) which is supported on a metal sieve; above the skin is an impermeable sheet of rubber or polythene, with a hole in the centre, through which liquids are introduced.

A differential pressure is exerted between the porous material and the membrane, the pressure on the porous surface being lower than that on the membrane. Acetone is passed through the skin under pressure until it is dehydrated; the pelt is then tanned with a solution of 100 parts saturated chromic chloride in methanol and 500 parts acetone, plus saturated aqueous ammonia.

Tannage is claimed to be complete in a few minutes, when the tanning solution remains green after passing through the skin.

It may be recalled that in 1942 a provisional patent specification was taken out by the B.L.M.R.A. for a method in which pelt was dehydrated by treatment with acetone, followed by removal of the water and solvent by evaporation.

—*Lea. Tr. Rev.*, 122, 3686, 312, (1956).

**TANNING.** *Boehme Fettchemie*. BP 755, 331. *Via. J.S.D.C.*, 72, 11, 555, (1956). Emulsions made by the process of BP 753, 668 (cf. *J.S.D.C.*, 72, 493 (Oct. 1956)), using a polyalkylene oxide wax of mol. wt. 2000, a non-sulphonated oil, and an inorganic tanning agent, are particularly suitable for a combined brush-tanning and fatting of hides. They are very stable and may be added to a chrome tanning liquor. Their use gives full-handling leathers without need for separate fatliquoring.

**WET TREATMENT OF ANIMAL SKINS.** *Secotan*. B.P. 755, 969. *Via. J. Soc. Dyers & Col.* 72, 11, 555, (1956). The skin is placed on a porous bed and then a thin flexible, preferably electric, membrane is laid over the entire bed, and fluid pressure is applied to the membrane to force it against the bed. The treating liquor is then introduced under pressure between the skin and the membrane, this pressure being sufficient to cause the liquor to cover the skin but insufficient to separate the membrane from the parts of the bed not covered by the skin, the pressure on the membrane being kept up during the whole of the treatment.

**TANNING AGENTS.** B.P. 756, 481. *J. Soc. Dyers & Col.* 72, 11, 555, (1956). The products obtained by condensing hydroxymethyl compounds of dicyandiamide and/or of dicyandiamidine with polyhydric phenols in acid medium at  $> 50^{\circ}\text{C}$ . when used in tanning yield leather of light colour which can be dyed and greased like chrome-tanned leather.

#### NOTES AND NEWS

**EAST AFRICA INTRODUCES A PORT INSPECTION SERVICE FOR HIDES AND SKINS.** Tanners are benefiting from the East African drive to improve hide and skin quality. Suspension drying now used for 99% of sheepskin exports, 97% of goatskins and 96% of hides has raised the value of East African material. Efforts to cut out excessive branding and to eliminate putrefactive damage are being stepped up. New port inspection service is preventing the export of hides and skins that are clearly undesirable.

—*The Lea. Tr. Rev.* 122, 3681, 201, (1956).

**PROCESS PREVENTS WOOL DAMAGE IN CARBONISING.** Damage caused to wool in carbonising can be avoided by a process developed by the Commonwealth Scientific and Industrial Research Organisation.

The Process requires the addition of a wetting agent to the sulphuric acid bath used in carbonising. Although the acid destroys the grass seed and other vegetable matter adhering to the wool, it also attacks the wool fibres.

The C.S.I.R.O. has found that all types of wetting agents offer some protection to wool and that the quantity required depends on the efficiency of the scouring.

The most satisfactory material tested in a non-ionic wetting agent known as Lisapol NX; 0.03% of it may be added to the acid bath with an efficient scour. The addition of one pound of the substance for 200 pound of greasy wool would be sufficient.

—*Technical Newsletter issued by Aust. Govt. Trade Commissioner, Bombay.*

**SPECIAL LEATHER SHOES.** A solution to the problems associated with wearing rubbers or overshoes—hot, stuffy feet and the inconvenience of putting the rubbers on and off, is to wear work shoes treated with one of the special silicone products for leather. These products, when used in tanning the leather, provide lasting water repellency without clogging the pores in the leather through which the foot breathes.

—*Sewage & Ind. Wastes*, 28, 11, 1431, (1956).

**TWO NEW CHEMICALS BY ROHM & HASS.** Zircotan S, a sodium zirconium silicate, and Leukanol C, a condensed phenolic syntan, for use in the production of white-tanned leather have been developed by Leather Chemists of the Rohm & Hass Co., Philadelphia.

According to O. V. Weberbrand, manager of the Company's leather chemicals department, when these materials are combined in the tanning formulation, "the finished leathers exhibit improved temper, tighter break and brighter white".

—*Lea. & Shoes*, 132, 20, 54, (1956).

Leather tanning by the "oil tan" method of preparing buckskin and other leathers was originated by Talmadge Edwares in Johnstown, N.Y. in 1810.

—*Famous First Facts*, Joseph Nathan Kane, New York; *The H. W. Wilson Co.*, 1950. *Via. J.A.L.C.A.* 51, 11, 605, (1956).

Patent leather was tanned in 1819 at New York, N.J. by Seth Boyden at his tannery which he had established in 1813. At first, the varnish was dried in the sun, but later it was dried in a warm room. Still later, in 1820, he made an oven to hold sixteen skins.

—*Famous First Facts*, Joseph Nathan Kane, New York; *The H. W. Wilson Co.*, 1950. *Via. J.A.L.C.A.* 51, 11, 605, (1956).

A leather-splitting machine to split leather to any thickness was invented by Samuel Parker, of Billerica, Mass. who received patents on July 9, 1808 and April 26, 1809 on "currying and finishing leather". This invention doubled the use of leather.

—*Famous First Facts*, Joseph Nathan Kane, New York; *The H. W. Wilson Co.*, 1950. *Via. J.A.L.C.A.* 51, 11, 605, (1956).

## C. L. R. I. NEWS

1. Dr. Y. Nayudamma, Assistant Director-in-charge, participated in the 16th annual conference of the Association of Principals of Technical Institutions in India, held at Karaikudi on the 5th and 6th February 1957.

2. The following members of the staff have been promoted. Our congratulations to—

Mr. R. Selvarangan promoted as Junior Scientific Officer.

Mr. J. C. Deb promoted as Senior Scientific Assistant.

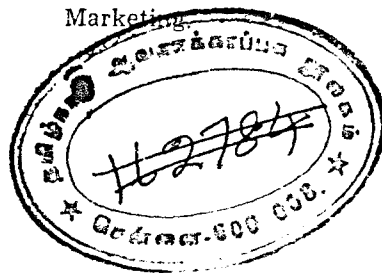
Under the auspices of the C.S.I.R. Club, the Central Leather Research Institute Staff Club got up a benefit dance performance by Srimathi Kamala Laxman and Baby Radha on the 29th January 1957. Shri P. M. Sundaram, Secretary, C.S.I.R., presided.

Central Leather Research Institute participated in the Madras University Centenary Exhibition at the Engineering College grounds, Guindy, held between 28-1-'57 to 17-2-'57.

The Central Leather Research Institute Staff Club participated in the Shanti Swaroop Memorial Tournaments conducted by the National Physical Laboratory, New Delhi.

## VISITORS

|                                                                                               |    |           |
|-----------------------------------------------------------------------------------------------|----|-----------|
| Sir Howard d'Egville, Secretary-General, Commonwealth Parliamentary Association, London       | .. | 1—2—1957  |
| Mr. S. T. Berkeley Hill, Messrs. D. J. Keymer & Co., Ltd., Bombay.                            | .. | 2—2—1957  |
| Mr. David E. Green, Enzyme Expert, University of Wisconsin, U.S.A.                            | .. | 4—2—1957  |
| Prof. F. A. Kaichev, Delegate to the Science Congress from the Peoples' Republic of Bulgaria. | .. | 6—2—1957  |
| Prof. J. C. Jakubowski, Delegate to the Science Congress from the Polish Academy of Sciences. | .. | 7—2—1957  |
| Staff & Students of the Presidency College, Calcutta.                                         | .. | 12—2—1957 |
| Senior Marketing Officer and 20 trainees in Agricultural Marketing                            | .. | 13—2—1957 |



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