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CENTRAL LEATHER RESEARCH INSTITUTE,
ADYAR, MADRAS-20.

A SYSTEMATIC STUDY OF FUNGI ON TAN
LIQUORS—I

Aspergilli

BY

V. S. KRISHNAMURTHI & S. N. SEN

(Central Leather Research Institute, Madras)

Received on 28th April 1958

SUMMARY

Eight species of Aspergilli, viz., *A. nidulans*, *A. variegator*, *A. carneus*, *A. japonicus*, *A. niger*, *A. flavus*, *A. terreus* and *A. unguis* have been isolated from tan liquors collected from the tannery of this Institute of which four are described here.

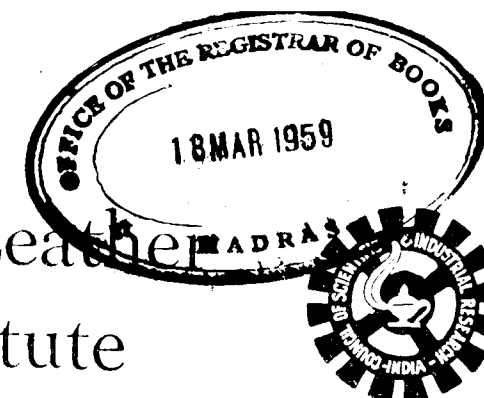
Four species of Aspergilli, viz., *A. nidulans*, *A. variegator*, *A. carneus* and *A. japonicus* isolated from the tan liquors of this Institute are described. In addition to these, *A. niger*, *A. flavus*, *A. terreus*, and *A. unguis* which have been already described on leather^{1, 2} are also recorded in tan liquors.

Records of the different species of Aspergilli mentioned in this paper occurring either on tan liquor or leather are shown in the following table:

	Tan liquor		Leather
	Recorded now	Recorded earlier	Recorded earlier
<i>A. nidulans</i>	+	—	Martin ¹⁰
<i>A. variegator</i>	+	—	—
<i>A. carneus</i>	+	—	—
<i>A. japonicus</i>	+	—	—
<i>A. niger</i>	+	Knudson ³	Krishnamurthi ¹ Musgrave ^{4, 5} Cordon ⁶ Wilson ⁷ I.R.I.C. ⁸
<i>A. flavus</i>	+	George ⁹	Krishnamurthi ¹ Musgrave ⁵ Cordon ⁶ Krishnamurthi ² Musgrave ⁴ Cordon ⁶ Krishnamurthi ² I.R.I.C. ⁸
<i>A. terreus</i>	+	—	—
<i>A. unguis</i>	+	—	—

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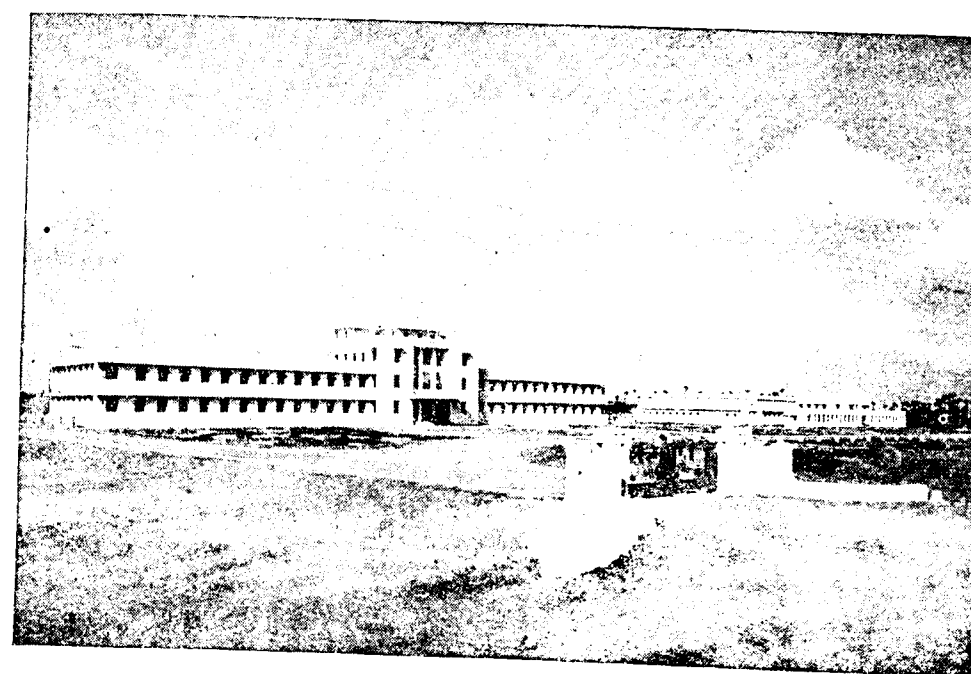


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INDIA

From the above table, all the species except *A. niger* and *A. flavus* have been recorded for the first time in tan liquors at this Institute.

The following descriptions are based on cultures grown on Czapek's solution agar.

11. *A. nidulans* (Eidam) Wint. in *Rab. Krypt.-Fl.* 1²: 62, 1884; Thom and Raper, *A manual of the Aspergilli*, p. 156, 1951.

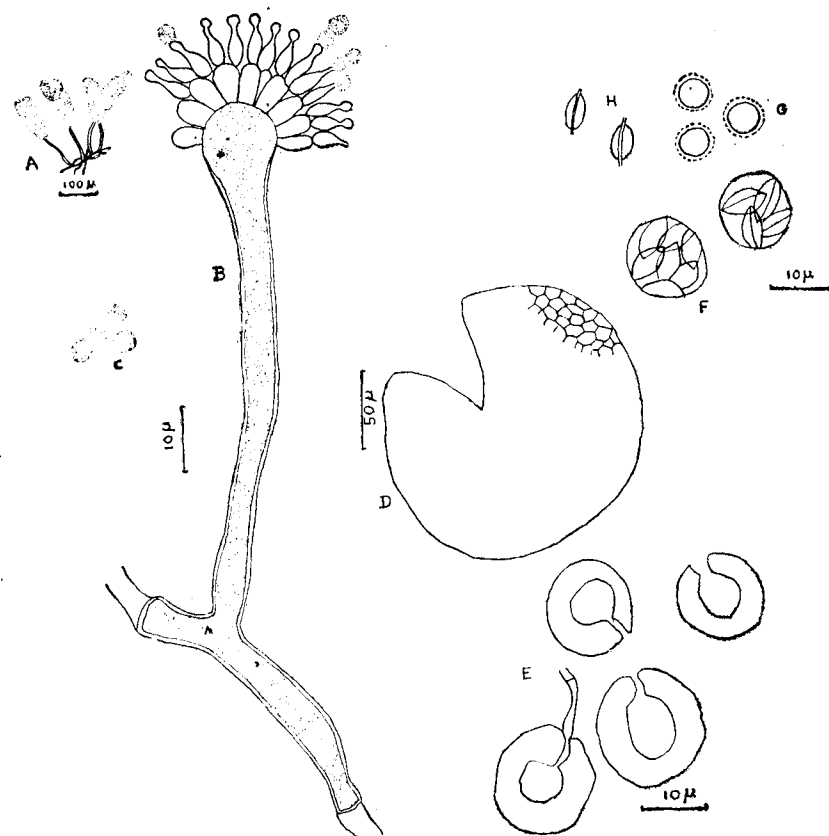


FIG. 1. *A. nidulans*: A—Portion of colony; B—Conidial head; C—Conidia; D—Perithecialium; E—Hülle cells; F—Ascus with ascospores; G—Ascospores in face view; H—Ascospores in profile view.

Colonies fast growing with abundant production of conidial and perithecial structures. Cultures present sage green (22 I 3)¹¹ or Leek green (22 J 5) colour. Conidial structures are followed by abundant production of perithecia

which present a granular or corrugated appearance of the colony, the colour of which changes to Racquet (15 C 7). Reverse in shades of purplish red (54 E 3).

Conidial heads columnar, conidiophores smooth, sinuous, short, in shades of pale brown, measuring 29.5 to 129.8 μ in length and in diameter 3.5 to 7 μ at vesicular end and 3.5 to 5.9 μ at the foot-cell end. Vesicles hemispherical to sub-globose, brown, fertile on the upper half only. Sterigmata disposed in two series, primaries 4.7 to 7.0 × 2.4 to 3.5 μ, average 5.8 × 2.8 μ; secondaries 5.3 to 7.7 × 2.1 to 3.0 μ, average 6.6 × 2.7 μ. Conidia globose, rough, green in mass, hyaline to sub-hyaline, individually 3.0 to 4.1 μ, mostly 3.5 μ, average 3.1 μ.

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Perithecia, globose to sub-globose 88 to 380 × 80 to 320 μ surrounded by thick walled hülle cells measuring 8.3 to 23.6 × 7.8 to 21.2 μ in diameter. Walls of the perithecia break up liberating ovoid to globose asci measuring 8.3 to 10.6 × 2.7 to 9.4 μ; average 10.3 × 6 μ. Ascospores lenticular, purple-red with prominent equatorial crests leaving in between a furrow; margin of the crests entire or sub-undulate, measuring less than 1 μ in width. Ascospores (overall dimensions) 4.5 to 5.4 × 3 to 3.5 μ, mostly 5 × 3.5 μ, average 4.8 × 3.5 μ.

12. *A. varicolor* (Berk. and Br.). Thom and Raper, in *Mycologia*, 31: 663-667, 1939; Thom and Raper, *A Manual of the Aspergilli*, p. 163-166, 1951.

Colonies moderately fast growing, mycelium submerged, aerial mycelium scanty, perithecia clustered towards the middle of the colony. Cultures garland gr. (22 H 7) to yew gr. (24 L 1). Reverse uncoloured in the beginning, turning deep purple at perithecial areas Cyclamen (47 L 9) to (48 L 12) and dilute purple at other parts (54 E 3).

Conidial heads abundant, columnar, green. Conidiophores smooth, brownish, measuring 130 to 450 μ, in

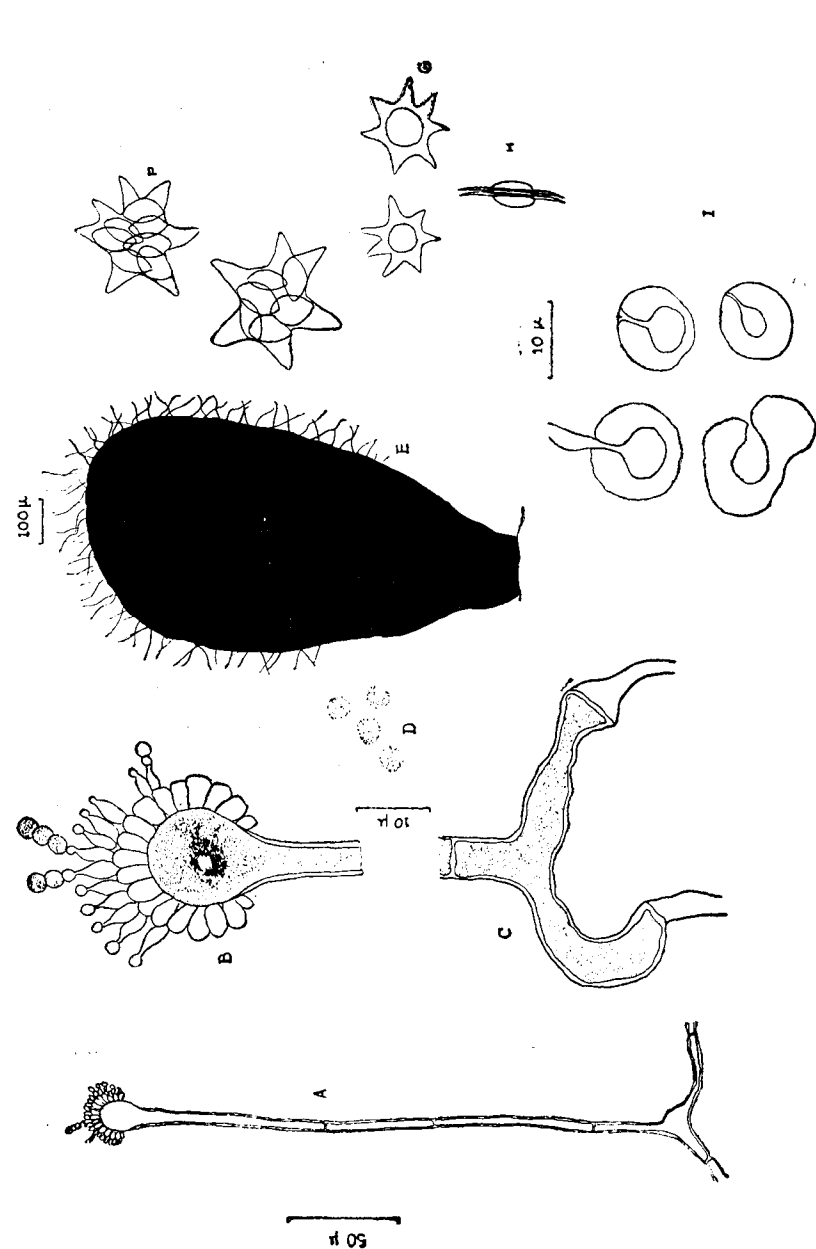


FIG. 2. *A. variegator*: A — Conidial head; B — Head enlarged; C — Foot-cell; D — Conidia; E — Pseudostalked perithecia; F — Ascus with ascospores; G — Ascospore in face view; H — Ascospore in profile view; I — Hülle cells.

diameter 3.5 to $6\ \mu$ at the vesicular end and 2.5 to $5\ \mu$ at the foot-cell end. Vesicles hemispherical, pale yellowish brown in colour, 11.8 to 20.1×7.1 to $2.0\ \mu$ in diameter, fertile over the upper half only. Sterigmata in two series, primaries 6 to 9×3 to $4\ \mu$, average $7.1 \times 3.2\ \mu$; secondaries 5 to 9×2.4 to $3.5\ \mu$, average $7.1 \times 3.0\ \mu$. Conidia globose, rough, green in mass, 3 to $3.5\ \mu$, mostly $3.5\ \mu$, average $3.2\ \mu$.

Perithecia in clusters, globose or pyriform, with a pseudostalk, measuring up to $700\ \mu$ long with $500\ \mu$ in diameter, surrounded by hülle cells measuring up to $30\ \mu$ in diameter. Asci oval to spherical 9 to 14×7 to $12\ \mu$, average $11.5 \times 9.1\ \mu$. Ascospores purple red, lenticular, with two prominent equatorial crests, slightly curved, cut into teeth; spore body measuring 3.5 to 4.1×3 to $3.5\ \mu$, average $3.7\ \mu$, mostly $3.8 \times 3.0\ \mu$. Crests measuring up to $4\ \mu$ in width.

13. *A. carneus* v. Tiegh, in Bull. Soc. Bot. France **24**: 103, 1877; *A. carneus* Blochwitz, in Ann. Mycol. **31** (1/2): 81, 1933; Thom and Raper, *A Manual of the Aspergilli*, p. 201-202, 1951.

Colonies moderately spreading, more or less floccose, mycelium submerged, from white or (11 A 1) to Flesh (11 A 2) with the age of the culture. In 20% sucrose from Bisque (11 A 3) through Peach (9 A 5) to Venetian pink (2 E 7) or Rose d'Althoea (1 I 7).

Heads columnar and abundant, conidiophores long, smooth, uncoloured, sinuous, measuring 221.8 to $762.8\ \mu$ long and 2.1 to $5.3\ \mu$ at the foot-cell end and 2.4 to $7.0\ \mu$ at the vesicular end in diameter. Vesicles hemispherical, fertile at the upper half only, measuring 5.3 to $14.7\ \mu$ in diameter. Sterigmata in two series, primaries measuring 5.6 to 7×2.1 to $2.4\ \mu$, average $5.4 \times 2.2\ \mu$; secondaries 5.3 to 5.9×1.8 to $2.4\ \mu$, average $4.9 \times 1.8\ \mu$. Conidia smooth, colourless, globose to sub-globose, 2.4 to $3\ \mu$, mostly $2.4\ \mu$ and average $2.7\ \mu$.

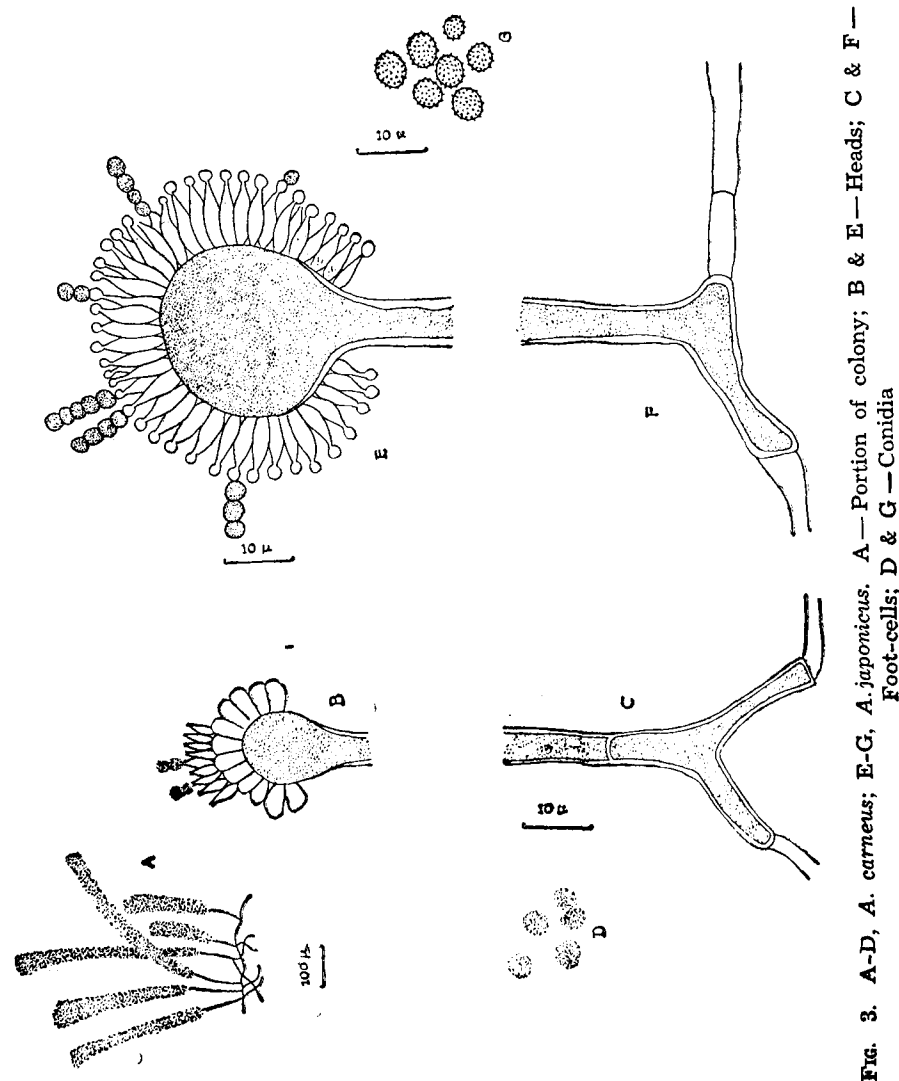


FIG. 3. A-D, *A. carneus*; E-G, *A. japonicus*. A—Portion of colony; B & E—Heads; C & F—Foot-cells; D & G—Conidia

14. *A. japonicus* Saito, in Bot. Mag. (Tokyo) 20: 61, 1906; Thom and Raper, *A Manual of the Aspergilli*, p. 230-231, 1951.

Colonies fast growing and spreading with profuse conidial heads, sporing heavily with abundant submerged mycelium, sporing areas Spanish Raigin (48 L 3) to deep purple-brown in colour (48 L 12). Reverse uncoloured, occasionally yellowish brown (14 K 7) with age.

Conidial heads globose, splitting radially. Conidiophores smooth, brownish in colour, measuring 250 to 1500 μ , in diameter 5.9 to 15 μ . Vesicles globose, 22 to 70 $\times$ 20 to 60 μ . Sterigmata all over the surface of the vesicle in single series measuring 6 to 9.5 $\times$ 3.5 to 8 μ . Conidia globose, echinulate, brown in colour 4 to 5.3 μ , mostly 4.7 μ , average 4.3 μ . Sclerotia were not observed.

Acknowledgement

Thanks are due to Dr. V. Agnihothru, formerly of the Botany Laboratory, University of Madras, and now Assistant Mycologist, Tocklai Research Station, Assam, for the help in the identification.

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Finishing:

Natural chrome soles: The sides are finished as natural chrome soles by applying a paste of 5 parts Barytes, 5 parts China clay and 1 part gum Arabic, on the flesh side and a paste of 5 parts of gum and 1 part of China clay on the grain side.

Waxed chrome soles: The sides are finished as waxed chrome soles by dipping the dried sides in molten paraffin wax, the temperature being 80-85°C. A small quantity of tallow or rosin may be added to the paraffin wax, if necessary. The sides are kept dipped for about 5 minutes, that is, till no more bubbles come out of the sides. After dipping, each side is drained and cooled and weighed.

Yield: (Unwaxed)—40-45% on fleshed pelt weight.

(Waxed) —50-54% „ „ „ „

TECHNICAL SEMINAR

Studies on chrome liquors — Effect of addition of organic salts to SO₂ reduced liquors*

K. R. V. THAMPURAN

The effect of addition of masking salts to sulphur dioxide reduced chrome liquor has been studied. The salts tried are acetate, citrate, formate, phthalate and tartrate of sodium. The effect of addition of these salts to the pickle also has been studied. The results obtained in experiments with hide powder and pelt pieces, are being further confirmed with large-scale tannery experiments.

*Summary of the talk on 5-12-1958.

RESEARCH BEARS FRUIT

Practical Demonstration No. 8

(Second Series)

Manufacture of Natural and Waxed Chrome Sole Leather on a
Cottage and Small Scale Level*

BY

M. A. RAMA IYER, K. RAJABATHAR & K. T. SARKAR

Raw Materials : Wet-salted buff hides weighing 40-50 lbs. each.

Soaking : The hides are weighed and soaked in plain water for three hours and then 3-4 quick changes of water are given. They are piled up to drain and cut into sides.

Unhairing by Painting : An unhairing paint is prepared as follows :—

Sodium sulphide (fused) 1% on wet-salted wt.

Slaked lime 10 % do.

Water 8% do.

The sides are dipped in the above paint and piled up.

Reliming : Next day, the sides are unhaired and relimed with 1% caustic soda and 10% slaked lime (on wet-salted weight) and enough fresh water in a pit. The remaining paint paste, if any, may be added to the pit. The sides are handled twice daily, for 4-5 days.

*Process demonstrated in Dec. '58/Jan. '59.

Fleshing : The sides are then fleshed and the weight noted. The fleshed sides are kept in water overnight and next day, they are given two or three changes of water and then scudded.

Deliming and Pickling : After scudding, the sides are given two or three changes of water and delimed with 1% of ammonium sulphate (on fleshed weight), the sides being trampled for half an hour. Then they are scudded, washed and pickled with 1-1½% sulphuric acid, 10% salt and 100% water (on fleshed weight). The sides are trampled in the pickle solution for half an hour and left overnight in the pickle bath.

Chrome tanning : Next day, the sides are trampled for 20 minutes and put in a fresh pit with ½ pickle liquor, 2/3 fresh water, 4% salt (based on fleshed pelt weight) and 1/3 of the total chrome liquor required. (The chrome liquor is prepared the previous day with 100 lbs. of sodium dichromate, 200 lbs. water, 83 1/3 lbs. sulphuric acid, and 66 2/3 lbs. molasses. After complete reduction of the dichromate, the liquor is made up with water to a total weight of 300 lbs. For every 100 lbs. of the fleshed pelt weight 18 lbs. of this liquor is used). The remaining 2/3 chrome liquor is then added in two instalments in an interval of two days. The sides are daily handled, slicked and piled. When the chrome liquor is completely struck through, the bath is basified by the addition of half a percent sodium carbonate (on fleshed weight) dissolved in water and added slowly. The sides are handled in the basified chrome liquor for 2 or 3 days and piled up for two days (the leather should stand a five-minutes boiling before being piled).

Washing and neutralising : The sides are weighed, washed, neutralised with 1% sodium bicarbonate and again washed and oiled with 2% T.R.O., the latter being applied on both grain and flesh sides. The sides are then nailed out on boards and allowed to dry completely.

TECHNICAL SEMINAR

Use of Alkyd Resins in Leather Finishes*

T. K. PARTHASARATHI

The present investigations have been undertaken with a view to formulate a leather finish based on alkyd resins, that could be straight away applied to leather to produce a smooth and glossy finish. Rosin-maleic anhydride resins, modified with linseed oil, have been tried in the first instance and the optimum proportions of the ingredients have been worked out. While rosin-maleic alkyd resins are superior to glycerol-phthalic-linseed resins in gloss, they are inferior in durability. So, blends of rosin-maleic alkyd and linseed-glycero-phthalic anhydride resins have been investigated. Temperature and duration of, cooking the product played a very important part in the formulation of these finishes. When pigments are used along with these cooked resin finishes, increased drier concentration has been found necessary. The pigmented alkyds so obtained can be applied on leather by means of a fine piece of cloth or brush and the levelling up done by a spray coat. Resin finishes of this type can be easily emulsified. Emulsion alkyds are economical and being water-based, water soluble dyestuffs and pigments could be incorporated in them.

*Summary of the talk given on 19-12-1958.

CLASSIFIED ABSTRACTS

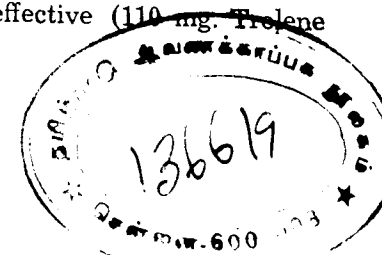
RAW MATERIALS

THE DAMAGE TO HIDES BY ARTHROPODS. *Miroslav Tomásek (Ministry for Consumer Goods Ind., Prague) ... Kožarstvi 7, 61-3 (1957); Chem. Abstr. 52, 15941 (1958).* The damage by various arthropods to hide during the life of the animal causes 63% of total hide defects. Damages by biting and sucking lice and by *Amites* are described. Washing of animals with 1% solution of DDT or HCH is useful. Spraying the entire surface of animals with a solution of colloidal S in a 7% solution of K soap repeated for 5 weeks gives good results. The damage to the grain of leather can be minimised by buffing.

WAR ON THE CATTLE GRUB—PAST PRESENT AND FUTURE. *Fred O'Flaherty. Leather Manufacturer, 75, No. 5, 1 (1958).* There are two distinct species of cattle grub—*Hypoderma bovis* and *Hypoderma lineatum*. The grub corresponds to the adult larva stage of the warble fly, which spends its entire larva period on the host animal. Though the grub starts its life on the legs of the animal, where the eggs are laid, it later penetrates into the animal's skins and migrates to different parts of the body molting several times. The final abode is in the subcutaneous tissue of the skin in the back region; the larvae, however, have been found in the gullet and in various tissues. In the last stages the presence of the grubs is shown by large swellings on the hide surface. The larvae spend 9-10 months in the cattle.

The losses brought about by the grubs begin on the farm and continue in the dairy herd, packing houses and the Tanning Industry. The total animal loss in U.S.A. is placed at 200 million dollars. With the laying of eggs on the cattle, loss of weight, loss of milk production, injury and crippling have been reported. Growth is stunted. At the site of the larvae entrance and in the grub's space, microbial infection and abscesses could occur. If the grubs are crushed and absorbed into the blood, a severe anaphylactic reaction could set in.

Tests with Dow product (ET-57) 'Trolene', at Texas, have shown that the drug was nearly 100% effective (110 mg. Trolene



being used per 1 kilo of live weight), there being 94.7% reduction of grubs before the larvae reached the subcutis of the back. Better gain in weight and savings in feed also resulted from the treatment. A Bayer product, Bayer 12/199, 'Neguvon' has been reported to be effective both when administered orally and when applied as a spray — an oral dosage followed by spray being recommended.

Grub damaged hides do not respond well to curing with salt. Though grub holes and spaces in the hide heal, the scar tissue is weak. Strap and sole leather are weakened by grubs. Grubby hides cannot be used for upholstery leather.

— V. S. P.

PROCESSES PRIOR TO TANNING

MODERN DEVELOPMENTS IN BEAMHOUSE PROCEDURE. *Thomas C. Thorstensen. Leather Manufacturer*, 75, No. 1, 20 (1958). The relative differences in solubility of the various protein constituents of the skin are of greatest importance in beam-house operations. While the soluble proteins are removed in the soak and in the lime, efforts are concentrated, in unhairing, on removing keratin, the collagen structure being disturbed as little as possible. For solubilising keratin and removing hair, two distinct unhairing systems are available. One using larger quantities of the reducing (sharpening) agent and the other, smaller quantities of the same. In the former, the hair is destroyed from the hair tip to the root; in the latter the hair is removed with the root. At the pH range of 12-13 at which the liming system of unhairing is carried out, there would be a swelling distortion of the fibres. A mixture of sulphide and sulph-hydrate is utilised by some, to effect the desired degree of swelling.

For progress in unhairing methods, a departure from the lime method is necessary—unhairing below pH 12. Researches at Lowell have led to chemical systems which unhair under mild conditions, by which it is possible to unhair green salted cattle hides 2-4 hrs. after soaking.

Enzymatic unhairing would seem to be the ideal method of removing hair. Development of enzyme depilants, involves obtaining specific enzymic activity by control of pH and addition of chemicals. By applying a few thousandths of one per cent, in solution,

of commercially available enzymes, it has been possible to unhair cattle hides, goatskins or calfskins overnight, the costs being greatly cut down.

— V. S. P.

DISCUSSION OF BEAMHOUSE PROCEDURE. *R. E. Davis. Leather Manufacturer*, 75, No. 5, 30 (1958). Two distinct types of beamhouse procedures are discussed. The fast process is used where both drum and paddles are available. Soaking is achieved in 4 hours, at 75-80°F using sodium tetrasulphide; a twenty-minute wash in the same drum or paddle follows. 3% sodium sulphide or a combination sulphide and sulph-hydrate is added. After running for 15 minutes, 3% hydrated lime is added. After two hours (with occasional turnovers in this time) a steady 30 minutes run is done. The hair is now pulped and the epidermis separated. After draining and a one-hour wash, reliming is done for 15 hours at 75°F, with addition of 5% hydrated lime. Fleshing, bating, pickling and tanning follow. The total time for soaking, unhairing and reliming by this 'fast' process is 24 hours.

The slow process (for the same types of leathers) is used where paddles or vats are available. Green-salted hides are washed, fleshed, soaked overnight with or without sodium tetrasulphide, at 65°F. 0.3% Flake sodium sulph-hydrate and 8-10% hydrated lime are added and the hides left in this for 5 days, at temperatures of 65-70°F. Unhairing, scudding, fleshing, bating, pickling and tanning follow. The total time by this slow process for soaking, unhairing and reliming is 6 days.

In the fast process, the insufficient water absorption, decrease in the internal surface of the fibres and the slow removal of soluble proteins, due to short soaking, are compensated for by more mechanical agitation and increased temperature; due to the high concentration of sulphide together with lime, hair is completely dissolved from the surface, the action being too fast, for the hair bulbs to be affected, which are consequently left under the grain. The alkali produced by hydrolysis of sulphide would cause non-uniform swelling, apt to produce grainy or drawn leather. Sodium sulph-hydrate does not hydrolyse and forms less NaOH when added to lime; the pH is lowered. Because of its specific action on keratin the sulph-hydrate makes possible a more complete separation of keratin from collagen, causing little damage to hide substance. High concentrations of sulphides with lime increase saponification of fats.

The slow procedure would require more machinery; the cost of chemicals in the fast process would be ten times greater than in the slow one. In the slow one, saleable hair is recovered (the further processes of removal of hair and paddling would increase the cost of hair removal).

The two processes are two extremes and a middle-of-the road course is recommended.

— V. S. P.

VEGETABLE TANNING

THE TANNINS OF PINUS RADIATA. *H. Anderson and A. Bilkens. Australian Journal of Applied Sci.* **9**, 183-91 (1958); *Chem. Abstr.* **52**, 15105 (1958). The bark contained tannin 18.2, soluble nontannin 3.8, moisture 14.0, insolubles 64.0%. A liquor was prepared by a 4-stage countercurrent extraction, cooled and settled overnight, decanted and concentrated to sp.gr. 1.150. This liquor formed a sludge on dilution. It had a pH of 3.9 and gave a dark, slightly reddish leather. On maintaining the liquor 48 hrs. at 18-12° a marked improvement in color was noted; there was some further improvement on maintaining at 12-2°. Minimum sulfiting conditions to render the sludge soluble were 4% Na_2SO_3 on solids at 8 lb. steam for 45 min. Tannage tests with liquor clarified by chilling were run in parallel with wattle tannin. *Radiata* tan gave a slightly higher yield (significant only at the 10% level) and a slightly firmer leather.

IMPORTANCE OF WATER SOLUBLES FOR THE EVALUATION OF QUALITY AND KIND OF TANNAGE OF VEGETABLE-TANNED SOLE LEATHER. *Anton Blazej (Tech. Univ. Slovakia, Bratislava), Kozarstvi* **7**, (1957); *Chem. Abstr.* **52**, 15105-6. (1958). Slow tannage is defined as a 6-12 month tannage in cold liquors of 28-35° Barkometer. Leather thus tanned should contain up to 10% water-soluble matter (*I*). Yearly Averages. (1946-55) for *I* in Czechoslovak slow-tanned leather were: bends 6.7-8.8, shoulders 8.3-10.8, bellies 9.4-11.3%. Corresponding values for combination-tanned leathers were 11.9-14.3, 13.4-15.8, and 14.1-17.4%. The first Czech syntans K_1 and K_2 affected *I* unfavourably. Syntans K_1D and K_2D are better, but when the syntans comprise more than 30% of the total tannin the quality of the leather is impaired and *I* is increased. The high degree of sulfitation of spruce bark in extg. tannin also affects *I* unfavourably. When the authorized quantity of tannin used was increased from 32 to 36% of the pelt wt., with syntans comprising

25-30% of the total, the annual average. *I* declined from 13.6 to 12.8%. There has been an increase of *I* in slow-tanned leather but never to exceed 10%. The standards for *I* in sole leather proposed by Kubelka (15%) and Stather (12%) are needlessly high. Current Czechoslovakian standards for maximum *I*, bends 10, shoulders 12, bellies 14% for slow tannage, and 15, 17, and 19% for combination tannage, are fully justified. Best-quality sole leather contains 10-15% *I*. Comparison of standards of different countries is difficult because of differences and changes in methods of determining *I*. Abrasion resistance of sole leather cannot be predicted from its chemical composition.

CHROME TANNING

INFLUENCE OF THE VARIOUS BEAMHOUSE OPERATIONS, TANNING, AND FINISHING METHODS ON THE SURFACE YIELD OF CHROME-TANNED UPPER LEATHER. *Charles A. Danon. Commun. fac. sci. univ. Ankara* **7B**, 45-76 (1956) (in French); *Chem. Abstr.* **52**, 15942 (1958). A study was made by using and combining the normal manufacturing methods, to determine the best ways of increasing the surface yield of Cr-tanned upper leather without impairing its quality. Fourteen series of tests were carried out on a semi-industrial scale, each including 8 calf skins. The area, thickness, and weight of the skins were measured at each manufacturing stage, and the surface yield was calculated with respect to the soaked weight. The quality, physical properties, and chemical composition of the Cr-tanned upper leathers obtained from various tannages were also determined. Weak liming gave the largest surface yields. As_2S_3 -depilated leathers had an 88.5% surface yield and a high tensile strength; their appearance, however, was poor. The leathers which were dried under tension after fat-liquoring, gave an 87.5% surface yield; their tensile strength and appearance were fair. The leather tanned with phthalate-containing Cr liquors were of the best quality; their average surface yield was 80.4%, but their tensile strength was very high and their appearance was excellent. The Cr_2O_3 content, which varied from 3.90 to 5.58%, had no direct influence on the surface yield, tensile strength, and appearance of the leathers. The importance of determining SiO_2 in Cr-tanned leather is stressed.

OTHER TANNAGES

ZIRCONIUM TANNAGE I.—A COLORIMETRIC METHOD FOR THE DETERMINATION OF ZIRCONIUM IN LEATHER.

D. A. Williams-Wynn, *J.S.L.T.C.*, **42**, 360 (1958). This paper gives details of a colorimetric method for the determination of zirconium in leather which is suitable for either routine analysis or research and development work. Zirconium and sodium alizarin sulphonate give, in strongly acid solution, a red colour which is almost specific for zirconium. The colour formed in this way is very intense and tartrate has been found to reduce the colour intensity and to stabilise the system against precipitation.

THE FIXATION OF VEGETABLE TANNINS BY COLLAGEN TANNED WITH SULPHITO-CHROMIUM-SULPHATE. K. H. Gustavson, *J.S.L.T.C.*, **42**, 368 (1958). Pretanning hide powder with solutions of sulphito-sulphato-chromium complexes containing mainly uncharged complexes increases the irreversible fixation of vegetable tannins on subsequent retannage, compared with that obtained with untreated hide powder. Particularly on prolonged periods of vegetable retannage, the binding of vegetable tannins is exceptionally heavy. Large quantities of fixed chromium complexes are simultaneously displaced and part of the acido groups are removed. It is indicated that the additional binding of the constituents of the vegetable tanning extracts is mainly in the form of tannin-chromium compounds.

PROCESSES AFTER TANNING

WATER SOLUBLE CONDENSING RESINS IN LATEX BLENDS. P. Lyudvig, M. S. Monastyrskaya, S. A. Pavlov, G. K. Koshman and V. M. Chesunov. *Legkaya Prom.* **18**, No. 5, 22-6- (1958); *Chem. Abstr.* **52**, 15107 (1958). Addition of glyptal resins to latex SKS 30 up to 20% raises the strength of the sheet both in the raw and the vulcanized condition as shown by numerous plotted data. Such increase is due probably to the formation of a steric network with the chemical characteristics of bonds, confirmed by the almost identical values of some of its physical properties measured at 20° and 100°. Differences in results obtained on the addition of the glyptals to latex DVKhB70, such as lower strength of the raw sheet and higher values of the limit of stretch of the vulcanized sheet are evidently due to the specific properties of the latex itself. Use of these resins makes possible the elimination of casein as an additive.

CARBOXYMETHYLCELLULOSE. II. PREPARATION OF SODIUM CARBOXY-METHYLCELLULOSE by MULTIPLE-STAGE ETHERIFICATION. Eiji Hayakawa and Yazaemon Morita (*Govt. Chem. Ind. Research Inst., Tokyo*). *Tokyo Kogyo*

Shikensho Hokoku **53**, 37-75 (1958); *Chem. Abstr.* **52**, 15901 (1958). Na-CMC (carboxymethylcellulose) could be prepared no more advantageously by the double than single-stage process, when the degree of substitution (D.S.) was below 1.0, but with higher D.S. (1.5-2.0) the multiple-stage process was more economical in the amount of $\text{CH}_2\text{ClCO}_2\text{H(I)}$ required for carboxymethylation. In each stage, however, a minimum amount of I (about 0.8 mole/glucose unit) must be used, and the crude product must be thoroughly purified with 80% (or higher) MeOH or H_2SO_4 before proceeding to the next stage. Cellulose can be carboxymethylated under the optimum conditions either in a liquid-phase homogeneous or a solid-phase heterogeneous system, but the reactivity among the 3 OH groups of each glucose unit is about the same in either reaction. The latter reaction seems to be the more common one, as judged from available experimental data, involving rather complex inter and intramolecular reactions. The distribution of substituted groups in the carboxymethylated product, however, is uniform; that is, all the cellulose fractions, even those of varying degrees of polymerization, show nearly the same D.S.

BACTERIAL DEGRADATION OF CARBOXYMETHYLCELLULOSE. L. Jännes and O. Kivinen (*Laaketehdas Orio, O. Y., Helsinki*), *Suomen Kemistilehti* **30B**, 97-8 (1957) (In English); *Chem. Abstr.* **52**, 15901 (1958). Investigations on the causes of the reduction of viscosity of carboxymethylcellulose (CMC)-containing materials revealed the existence of microorganisms which attack CMC. A grampositive bacterium was isolated and its morphology is described. Rapid deterioration of CMC gels resulted from pure cultures in their solutions.

TESTING

A METHOD FOR THE RAPID CALCULATION OF TITRATION CURVES. Jiri Celeda (*Vysoka Skola Chem.—Technol., Prague*). *Chem. Prumysl* **8**, Suppl. 1, 12 pp. (1958); *Chem. Abstr.* **52**, 14407 (1958). The principles for the rigorous calculation of titration curves in multi-component systems are described taking into account the dilution of solutions during titration and the ionic activity coefficients. The method is illustrated on a 25-ml. solution containing NaOH 0.66, Na_2CO_3 0.96, and aniline 0.8/meq. which is titrated with 0.1N HCl.

ELECTROCONDUCTIVITY TITRATIONS OF MIXTURES OF SODIUM CARBONATE AND SODIUM BICARBONATE. C. P. Dhamnaey. *Bull. Geol., Mining Met. Soc. India*, No. 14, 1-7

(1955); *Chem. Abstr.* **52**, 14408 (1958). Electroconductivity titrations of mixtures of Na_2CO_3 and NaHCO_3 for commercial analyses where indicators are of no use were made with HCl about 10 times the normality of the alkali. The electroconductivity curves for these mixtures show 2 breaks; one corresponds to the point at which half the Na_2CO_3 is neutralized and the other to the point of complete neutralization.

DETERMINATION OF ALUMINIUM AFTER ITS ISOLATION WITH SODIUM HYDROXIDE AND SODIUM CHLORIDE. Tsui-Lin Chien (*Inst. Mineral Materials. Ministry Geol. Peking*). Hua Hsueh Hsueh Pao **23**, 324-9 (1957) (*English summary*); *Chem. Abstr.* **52**, 14419 (1958). A method of separation of Al from Ti and Fe with NaOH and NaCl is described. The separation is quite complete in a single treatment. The modified method of detection of Al is based on the work of Taylor. A known quantity of Trilon B is added to the separated Al solution and the excess Trilon B is back titrated with standard Al. Solution. Hematoxylin is used as an end point indicator. Results show that this method of separation and determination can be applied to materials-containing Al from 2 to 200 mg. with Fe and Ti up to 400 and 600 mg. respectively.

COLORIMETRIC DETERMINATION OF CHROMIUM WITH DIPHENYL CARBAZIDE. Boda Gavril. *Acad. rep. populare Romine, Filiala Cluj, Studi si cercetari, stint., Ser. I, Stinte mat. fiz., Chim. tehnice* **6**, 217-27 (1955); *Chem. Abstr.* **52**, 14420 (1958). A colorimetric method based on the estimation of the reaction product of CrO_4 — and diphenylcarbazide (I) appears to be the most sensitive method for the determination of small quantities of Cr in cast iron. When I is added in stoichiometric amount according to the equation of Babko and Palii, then the intensity of coloration ($\log I_0/I$) does not follow LambertBeer's law. The absorption is in function of the concentration of CrO_4 , according to the above mentioned law, only when I is used in a large excess. The optimum conditions for analytical work are described as: $(\text{H}^+) = 1 - 10 \times 10^{-2}\text{N}$, the molar ratio of CrO_4 — to I 1:100, and the photometric reading after 30 min.

DETERMINATION OF TRIVALENT CHROMIUM IN THE PRESENCE OF CHROMATE. R. W. Cline R. E. Simmons, and W. R. Rossmassler (*Union Carbide Nuclear Co., Paducah, Ky.*) *Anal. Chem.* **30**, 1117-18 (1958); *Chem. Abstr.* **52**, 14421 (1958). Pipet a 10-ml. sample into a 15-ml. centrifuge tube. Add 1 ml.

of 1% $\text{Al}(\text{NO}_3)_3$ solution and precipitate the $\text{Al}(\text{OH})_3$ with NH_4OH . Centrifuge and then wash with 1 ml. of water. Dissolve the precipitate in 4 drops of H_2SO_4 , dilute to 10 ml. and reprecipitate as before. Again dissolve the precipitate in acid and dilute to 25 ml. Take two 10-ml aliquots, reserve one, and proceed with the oxidation of the other. Add 30 drops of Br water. Then fade the Br colour to a faint yellow by adding 10 M NaOH dropwise, finally adding 5 drops in excess. Heat to $90-5^\circ$ for 15 min., then add 1:5 H_2SO_4 and 1 drop of phenol. To both the oxidized aliquot and the reserved aliquot add 1 ml. of diphenylcarbazide reagent (0.15 g. in 25 ml. of acetone and 25 ml. water), dilute to 25 ml. and determine their transmittance against a water blank at 540 m μ . The difference in the 2 aliquots represents the Cr (III) in the sample.

SPECTROPHOTOMETRIC ASSAY FOR SULFHYDRYL GROUPS WITH N-ETHYLMALEIMIDE. Nicholas M. Alexander (*Eastern Regional Research Lab., Philadelphia, Pa.*) *Anal. Chem.* **30**, 1292-4 (1958); *Chem. Abstr.* **52**, 14429 (1958). A rapid, simple spectrophotometric method for determining thiols with N-ethylmaleimide is presented. The reaction is observed at 300 m μ . Sulfhydryl solutions having concentrations as low as 0.0001 M can be assayed. The procedure has been used to determine sulfhydryl concentrations in a tissue extract and in whole blood. The reaction is carried out in 0.1 M phosphate buffer (pH 6.8) with 0.01 M N-ethylmaleimide and a sulfhydryl concentration between 0.0009 M and 0.0001 M. A 0.001M N-ethylmaleimide solution in buffer is also prepared and the absorbancies of both solutions are read. Solutions containing everything but N-ethylmaleimide serve as blanks. The difference in absorption between the reacted and unreacted N-Ethylmaleimide solutions is divided by the molar extinction coefficient of the compound this quotient is equal to the molar sulfhydryl concentration of the sample. Absorption measurements are made in 1-cm. matched silica cells. The concentration of reactants can be varied as long as the N-ethylmaleimide concentration is in 10% excess of the sulfhydryl concentration. The reaction can be carried out at neutral or acid pH, although it proceeds faster at neutrality.

INFLUENCE OF PROTEINS ON AMPEROMETRIC TITRATION. Mieczyslaw Wroński (*Univ. Łódź, Poland*). *Chem. Anal. (Warsaw)* **3**, 73-6 (1958); *Chem. Abstr.* **52**, 15627 (1958). Amperometric titration of protein in the presence of Cu salt with alc. solution of 8-quinolinol was made. Samples containing 4 ml. 1N NaOH + 6% NH_3 , 1 ml. 0.108M CuSO_4 and casein solution,

were prepared. They were diluted with 1% Na_2SO_3 to make a 50 ml. solution. The galvanometer (sensitivity $1^\circ = 10^{-7}$ amp. and resistance $R_2 = 2300$) were used. The voltage was 1.7 v. The results are presented in a table and a diagram. The linear relation between equivalent point of saturation and the amount of protein used remained unchanged, in agreement with theory. A similar relation was obtained also for gelatin.

THE DETERMINATION OF LONG-CHAIN, QUATERNARY AMMONIUM COMPOUNDS. *R. Neu. Fette, Seifen, Anstrichmittel* 59, 503-5 (1957); *Chem. Abstr.* 52, 15929 (1958). Cation-active halides can be determined quantitatively through the halide ion. A weighed portion of the cationic is dissolved in water in a volumetric flask, a known excess of 15% NaClO_4 is added by a pipet with vigorous agitation, the flask is heated in boiling water for 15 minutes, cooled to 20° , made to volume and filtered. An aliquot of the filtrate is titrated with 0.1N AgNO_3 , K_2CrO_4 being used as the indicator, to determine the excess ClO_4^- present.

RAPID METHOD OF ANALYSIS OF RESIDUAL LEATHER FAT LIQUORS. *J. Pore and B. Poirier. Oleagineux* 13, 397-402 (1958); *Chem. Abstr.* 52, 15941 (1958). Aqueous emulsions are split by acid, and the fatty material is determined volumetrically. Place 100 ml. of the filtered emulsion in a volumetric flask, the neck of which is graduated from 100 to 110 ml. at 0.1-ml. intervals. Add 1 ml. isoamyl alcohol, shake, then add 5-6 ml. H_2SO_4 (65° Bé.), and shake vigorously. Immerse 10-15 minutes in boiling water, cool to room temperature and read the volume of fatty material collected in the neck. This procedure is also applied with minor modifications to sulfated fats and oils, polyglycol esters, and polyoxyethylene condensation products. By assuming density is 0.8 for natural fats and 0.9 for synthetic products, the determinations agree closely with results of more rigorous and lengthy procedures. For some mixtures of synthetic nonionics and natural fatty materials separate phases are split out, permitting determination of each component type.

THEORY

THE ROLE OF CROSS LINKAGES IN THE SOLUBILIZATION OF INSOLUBLE COLLAGEN. Arthur Veis and Jerome Cohen (Armour & Co., Chicago). *J. Phys. Chem.* 62, 459-62 (1958); *Chem. Abst.* 52, 14284 (1958)—The entropy of activation for the solubilization, $\Delta S^\ddagger$, of the native, intact structure (45.6 e.u.) is much smaller than the $\Delta S^\ddagger$ for thermal shrinkage (361 e.u.)

whereas $\Delta S^\ddagger$ for the solubilization of the disorganized structure is -62.9 e.u. Thus, the inhibition of solvent is very important in the activation step. There is no direct relation between the contraction temp. T_s and the rate of solubilization, although in solvent for which T_s is lowered the rate of solubilization is increased, even at $T < T_s$. Units of varying solubility exist in what is normally termed "insoluble collagen". Interchain linkages other than H bonds are primarily responsible for the insolubility of collagen; different distributions of these cross-linkages occur; and these different distributions probably arise from the fact that the peptide chains in collagen are not identical in amino acid composition or sequence.

CALCULATION OF THE BOND INDEXES AND OF CHARGES IN THE PEPTIDE LINKAGE. Andrée Goudot. *Compt. rend.* 246, 116-19 (1958); *Chem. Abstr.* 52, 15613 (1958) — The lengths of the C-N and C-O bonds in the peptide linkage are calculated from the bond indices and the charges on the N, C, and O atoms. These values are then applied to the binding of a metallic ion to both the N and O of the peptide linkage within the complex, enzyme-metal-substrate. Diglycine is used, having 4 π orbitals to represent the free electrons in that linkage. The coefficients for each orbital and linkage are calculated and from these the length of the corresponding bond, by Gordy's equation: $N = aR^{-2} + b$. Gordy determined a and b as constants for specific bonds. N and R are the bond order and length, respectively. The coefficients are for CN 0.5720; CO, 0.6674 R before, and after cation polarisation, respectively, are: CN, 1.34 and 1.47 Å.; CO, 1.27 and 1.25 Å.; the charges for atoms N, C, and O are, respectively 1.7782 and 2; 0.5232 and C, 4186125; and -1.6984 and 1.5899762. Dipeptidase activated by Co^{+2} is a catalyst in breaking the peptide linkage. Co is assumed to be bound to the enzyme by 2 hybrid bonds and by 4 to the substrate; by NH_3^+CO^- , NH^+ , COO^- , and through the O and N of the peptide linkage for diglycine. As Co^{2+} in the hexavalent complex must have a 3d electron promoted to a 4d orbital, it can be held after polarization on a C-O, a π acceptor. Co^{2+} has become cobaltic, with $\text{N-Co}^{+++} = 2.68\text{Å}$. The structure of the enzyme complex is shown.

THE ISOLATION OF A NEW PROTEIN COMPONENT OF MUSCLE. Tien-Chin Tsao and Kai Hsu (*Acad. Sinica, Shanghai*). *Sheng Li Hsüeh Pao* 20, 189-90 (1956); *Chem. Abstr.* 52, 15608 (1958). A slow-moving peak was noted in the electropho-

retic pattern of crude preparations of tropomyosins. A heat-labile protein which gives rise to this gradient was isolated by (1) the removal of sarcoplasmic proteins from muscle brei with *M* citrate buffer, pH 5.1, with running tap water, (2) extraction of the washed brei with *M* citrate buffer, pH 5.1, and (3) the removal of traces of tropomyosin impurity by $(\text{NH}_4)_2\text{SO}_4$ fraction at pH 5.1. It is suggested that the new protein is the same as the borate-soluble pseudoglobulin of Perry and the non-myosin substance of Szent-Gyorgyi, *et al.*

THE EFFECT OF PERIODIC ACID ON PROCOLLAGEN. I. THE UPTAKE OF PERIODIC ACID, HEXOSES, AND OF HYDROXYLYSINE. Helmut Hörmann and Gerhard Fries (Max Planck Inst., Munich, Ger.), *Z. physiol. Chem.* **311**, 19-28 (1958); *Chem. Abstr.* **52**, 15621 (1958). Pro-collagen, which probably differs from collagen by being less cross-linked, was obtained from calf skin. A solution of 700 mg. in 80 ml. 10% AcOH was treated with 10 ml. 0.2*M* NaIO₄. H₂O was added to make 100 ml. and the mixture was placed in the dark in a water bath at 20-40°. A comparison of N determinations, before and after dialysis showed that there was no breaking up of peptide chains after 72 hours at 40° or 250 hours at 20°. The authors conclude from this that the solubility of collagen in HIO₄ at temperatures over 40° is due to destruction of cross linkages rather than degradation of the protein. The uptake of HIO₄ was found to be 2.8 mols./100 moles amino acids. Hexoses were destroyed rapidly, but not completely, while the α -HN₂- and OH-groups of hydroxylysine were oxidized at a slower rate. The HCHO and NH₃ liberated corresponded exactly to the amount of amino acid degraded. Treatment of the reaction mixture with Schiff's reagent produced a strong colour due to the formation of aldehydes from hexoses and hydroxylysine.

LIGNIN AND LIGNIFICATION. VII. THE FORMATION OF LIGNIN IN THE YOUNG PLANT. 3. Hisao Ishikawa, Katsumi Takaichi, Sigeki Kitagawa, and Tae Oki (Ehime Univ., Matsuyama). *Nippon Nôgei-Kagaku Kaishi* **31**, 375-9 (1957); *Chem. Abstr.* **52**, 15657 (1958). Lignin (*I*) and other components were determined on young plants of *Phaseolus mungo* and *Pinus densiflora* during growth in water culture; effects of several organic compounds on *I* formation were established. Shikimic acid (*II*), phenylalanine (*III*), tyrosine (*IV*), phenylpyruvic acid, *p*-hydroxyphenyl-pyruvic acid, ferulic acid, coniferin (*V*), and syringin (*VI*) acted as precursors for *I*. Addition of these precursors to the

medium promoted *I* formation. VIII. THE FORMATION OF LIGNIN IN THE YOUNG PLANT. 4. Hisao Ishikawa and Katsumi Takaichi, *Ibid.* 380-3. Leaves of *Robinia pseudo-acacia* and seedlings of *P. mungo* were extracted with cold 0.1 *N* phosphate buffer of pH 6.5, and the presence of *I* precursors in the extracts was determined with paper chromatography. *II*-phosphate, sedoheptulose phosphate, *V*, *VI*, and coniferyl alcohol were found in the extract in addition to *II*, *III*, and *IV*. The extract was incubated with one of the precursors for 5 days at 30°, and a fraction insol. in AcOEt and soluble in dioxane (*I*-like substance) was obtained from the precipitate formed during incubation. The yield of this fraction was increased by *II*, *III*, *IV* or *V*; addition of powdered filter paper, peroxidase, and H₂O₂ also promoted the formation of *I*-like substance *in vitro*.

BYE-PRODUCTS

SUGAR CANE BAGASSE AS A FIBROUS PAPERMAKING MATERIAL. I. CHEMICAL COMPOSITION OF HAWAIIAN BAGASSE. S. B. Knapp, R. R. Watt, and J. D. Wethern (Crown Zellerbach Corp., Camas, Wash). *Tappi* **40**, 595-7 (1957); *Chem. Abstr.* **52**, 15058 (1958). Chemical analyses have been made on whole bagasse and on the pith and fiber fractions obtained by a wet separation, method from the 4 major varieties of Hawaiian cane. Extractives were low; Et₂O solubility 0.08-0.3%, EtOH-C₆H₆ solubility 1.6-4.7%, hot H₂O solubility 0.36-2.7%. There were more pentosans (25.8-8.8%) than in hardwood, and about the same amount of lignin (19.3-22.0%) and holocellulose (75.2-79.6%) as in hardwood. α -Cellulose content of the pith was 33.1-6.4%; of the fiber 41.9-3.3%; and of the whole bagasse, 36.5-8.8%. Ash content, which apparently was due mostly to dirt, was 1.83-2.36% in the pith, 0.63-0.82% in the fiber, and 1.25-19.6% in the whole bagasse. Chemically, the pith was quite similar to the fiber except in α -cellulose and ash contents.

PATENTS

FILAMENTS AND SHEETS FROM PROCOLLAGEN. Arthur Veis and Jerome Cohen (to Armour & Co.). U.S.2,838,363, June 10, 1958; *Chem. Abstr.* **52**, 15108 (1958). Filaments and sheets with relatively high wet strength are prepared from procollagen (*I*) by dialysis of an aqueous acid solution of *I* against H₂O at a rate slow enough to form an isotropic gel with a homogeneous appearance. The gel is then aged in H₂O to increase its cohesive

strength. An orienting stress is then applied; water was forced out. For example, the hide of a freshly slaughtered steer was chilled in ice water, cut into small pieces, washed with cold H_2O , frozen with Dry Ice, run through a hide splitter, and hair and untrimmed bits of flesh were split off. The pieces were rewashed, refrozen, thawed, washed in cold 10% NaCl solution, extracted with portions of ether, washed free of ether in cold water, and swollen in 0.1 ionic strength (pH 3.4) citric acid-Na phosphate buffer at 10° or lower. The I-containing supernatant liquor from the extraction was cleared by centrifuging to give a maximum I concentration of 0.5%. A dialysis bag filled with a 0.2% solution was suspended in a long glass tube through which cold water was flushed upward. Within 3 hours, the solution became turbid and within 5 hours, the gel had set. Dialysis was continued for 2 days, the bag was laid on a long strip of filter paper on a tilted board, both ends of the bag were cut off, and the gel was drained. The gel was hung vertically, water was forced out, and weights were hung on the bottom to keep it stretched. When dry, the filaments were approximately 0.008 in diameter, 48 in. long, had a tensile strength of 60 kg./sq.mm., and stretched approximately 10% before breaking in a standard suture-test apparatus.

CONDENSATION PRODUCTS OF POLYHYDRIC PHENOLS WITH HYDROXYMETHYLDICYANDIAMINE COMPOUNDS AS TANNING AGENTS. *Ernst Honold and Arthur Miekely (to Cassella Farbwerke Mainkur Akt.-Ges). U.S. 2,836,480, May, 27, 1958; Chem. Abstr. 52, 15942 (1948).* Skins are tanned by condensing in acid solution at 20-50°, 0.5-1 mole of a polyhydroxybenzene with 1 mole of mono-(hydroxymethyl) dicyandiamide or mono (hydroxymethylol)-dicyandiamidine, and using the resultant solution for tannage. Resorcinol and pyrocatechol are particularly useful. For tannage, 100 parts of unhaired skin is treated with 20-30 parts of the condensate in 100 parts of H_2O ; a 24-hour tannage is possible if the skins are not too thick.

RESINOUS SYSTEMS FOR TANNAGE. *Böhme Fettchemie G.m.b.H. Brit. 790,933, Feb. 19, 1958; Chem. Abstr. 52, 15943 (1958).* Watersoluble cationic resinous substances, e.g., an organic N compound containing amino or imino groups treated with an oxo compound, are allowed to react with the water-soluble salts of a polymeric inorganic or organic acid in contact with skins or hides. The system can be used as a pretannage or a retannage with HCHO, vegetable, synthetic, and chrome tannages. Urea-, melamine-, or dicyandiamide-HCHO condensates are particularly

cited, along with water glass or polymeric phosphates. Additional tanning substances, such as fatty tanning substances including alkyl sulfates, alkanesulfonates, alkylbenzenesulfonates, and-sulfonyl chlorides, in which the alkyl group contains ≥ 6 C atoms, can be added. The resinous system should contain 2-12% of the cationic condensate and 2-10% of the polymeric phosphate based on the skin weight when used as the sole tannage. From 2 to 10% of the condensate and 1-10% water glass may also be used. A white leather is produced with these agents alone or with 0.5-1% Cr_2O_3 in a combination tannage.

FIXATION OF WATER-BASED PIGMENT FINISHES ON LEATHER. *Badische Anilin & Soda-Fabrik Akt.-Ges. (Gerhard Otto, inventor). Ger. 849,995, Sept. 22, 1952; Chem. Abstr. 52, 15943 (1958).* Improved wet-rub fastness follows precipitation of anionic finish components with small amounts of cationic surfactants added to the usual top spray. Compounds with fatty-acid residues are preferred for the surface lubrication of the leather.

MILDEW-RESISTANCE OF LEATHER TREATED WITH BIS (4-NITROPHENYL) CARBONATES. *Sverre Dahl and Arthur M. Kaplan (to the United States of America, as represented by the Secy. of Commerce). U.S. 2,383,426, June 10, 1958; Chem. Abstr., 52, 15944 (1958).* A substantially mildewproof leather results from the use of 0.3-0.6% on the dry leather weight of bis (4-nitrophenyl) carbonate. The product is formulated for application in a solution containing bis (4-nitrophenyl) carbonate 5, dioxane 50, neatsfoot oil 10, and CHCl_3 35%. Bis (2-chloro-4-nitrophenyl) carbonate is equally effective. Tropical cabinet and field-exposure tests have demonstrated that these compounds are approximately as effective as 4-nitrophenol.

LIGNIN-PHENOL RESINS. *VEB. Farbenfabrik Wolfen (Alfred Rieche, Alfred Gnuchtel, and Kurt Junghans, inventors). Ger. (East) 11,150, Feb. 11, 1956; Chem. Abstr. 52, 15967 (1958).* Up to 50% of the phenol in phenol-HCHO resins can be replaced by alkali lignin (I). Thus, 100 parts of dry, atomized I was added to a mixture of 150 parts phenol and 3 parts 95% H_2SO_4 at 80° with stirring; SO_2 was evolved. The temperature was increased to 135° and, within 3 hours, increased to 170-80°. The mixture was maintained at 170-80° for 2 hours. Approximately 10 parts water and 3 parts phenol were distilled. The dark-brown product was cooled to 70°, stirred, and treated slowly with portions of 30% HCHO (total 100 parts), and 50% H_2SO_4 (total 10 parts).

During the period of addition the temperature was raised to 95°, and the mixture was refluxed at 95° for 3 hours. The resulting mass ought to be liquid at 95°, but should solidify on cooling to give a dark-brown, shining, hard, but slightly plastic resin which contains approximately 20% residual water. The water was not removed because it had plasticizing action and was evaporated on the rolls. The resin was crushed and processed with saw dust, hardners, etc., in a conventional way. The obtained pressed parts had a smooth surface.

AMIDES OF POLYUNSATURATED LONG-CHAIN DIBASIC ACIDS AND RESINOUS PRODUCTS THEREFROM. Geo. B. Payne, Curtis W. Smith, and Albert C. Muller (to Shell Development Co.). U.S. 2,832,799, Apr. 29, 1958; Chem. Abstr. 52, 15962 (1958). Novel amides are prepared by reaction of an amine with an unsaturated dicarboxylic acid formed by reaction of cyclic peroxides with compounds containing conjugated double bonds. For the preparation of 8, 12-eicosadienedioic acid (I), 50 parts 34% H₂O₂ was added to 98 parts cyclohexanone. The temperature was held below 40°. The mixture was allowed to stand at room temperature for one hour to form bis (1-hydroxycyclohexyl) peroxide (II), which was then dissolved in 750 parts MeOH containing 25 parts concentrated H₂SO₄, and 81 parts butadiene was added at 0° followed by a solution of 147 parts FeSO₄·7H₂O and 25 parts concentrated H₂SO₄ in 250 parts water. The temperature was held at 0° for two hours, the mixture was then heated to 65°, and the excess butadiene removed. Water (2 l.) was added and the solution was extracted with 300 parts C₆H₆ which was dried over anhyd. Na₂SO₄ and distilled. The C₆H₆ and unreacted cyclohexanone were removed and the residue boiled with a solution of NaOH for three hours. Acidification of the solution liberated an oily solid which was purified to yield I, m. 110-12°. m-Phenylenediamine (4-6 mole) and 0.27 mole of the dimethyl ester of I were refluxed at 150°. The MeOH formed was removed as it formed to yield N, N'-bis (3-aminophenyl)-8, 12-eicosadiene-1, 20-diamide (III), a brittle, black solid. Similarly, N, N'-bis (5-amino-2-azapentyl)-8, 12-eicosadiene-1, 20-diamide, an amber semi solid, was prepared from the di-Me ester of I and diethylenetriamine; the N, N'-bis (2-aminoethyl) analog, a viscous almost solid substance, from the di-Me ester of I and ethylenediamine; and the N, N'-diallyl analog, a solid from the di-Me ester of I and allylamine. 8, 12-Eicosadiene-1, 20-diamide, m. 172-4° (from EtOH), was prepared by treating I in C₆H₆ with oxalyl chloride,

concentrating the solution and adding 29% NH₃. The N, N'-bis (allylcarbonyloxy) analog was prepared from the di-Me ester of I and allyl chloroformate. Several castings were prepared by combining 40, 50 or 60 parts III with 100 parts polyether A (IV), and heating at 120° for 4 hours. IV was prepared by dissolving 2 moles bis-phenol in 10 moles epichlorohydrin and addition of 1-2% water to the mixture which was then brought to 80°. Four moles solid NaOH was added in small portions during one hour at 100°. After the addition, the water formed, along with most of the epichloro-hydrin was distilled off. The residue was combined with an equal amount of C₆H₆ and the mixture filtered. The C₆H₆ was removed to yield a viscous liquid, mol. wt. 350, epoxy equiv./100 g. 0.50. A coating composition was prepared by combining 60 parts III with 100 parts of IV and adding the mixture to a solvent containing xylene, BuOH, and methyl Cellosolve to form a composition containing 60% solids. This composition was then applied to Sn panels and the film cured at 120° to yield a coating which was hard, clear and had good flexibility.

GENERAL

LEATHER FUNGICIDES. Anon. *Leather Manufacturer*, 75, No. 7, 10 (1958). Main effect of mildew is the removal of greases from leather, causing stiffness and loss in tensile strength; most tanning agents and lubricants are susceptible to mildew. So to obtain a fungicide satisfying military needs more than hundred compounds have been studied by the National Bureau of Standards by (1) exposure of specimens containing known percentages of the fungicides on mycelial mats of *Aspergillus Niger* and (2) exposure in a tropical room. Salts of copper and iron, small amounts of HCl and high concentrations of neutral chloride are harmful to leather. Organically bound copper or chlorine is less harmful. Bis(4-nitrophenyl) carbonate and bis(2-Chloro-4-nitrophenyl) carbonate, two inert, colourless and water insoluble substances become poisonous to fungi only under mildew growing conditions. They are as effective as the corresponding nitro phenols; while 0.3% (by weight) of the bis compounds prevented mildew growth, upto 1.2% was not irritant to human skins. The 4-nitro-and 4-thiocyanophenols are the most effective of the compounds tested, their effectiveness appearing to be decreased by alkylation and increased by chlorination. 4-nitrophenol is permanent in leathers under non-leaching conditions, due to a combination of low volatility and fixation through hydrogen bonding. The bis carbonates also are not readily volatilisable.

The effectiveness of the bis compounds is due to their hydrolysis to nitrophenols, whose presence in leather has been established; the hydrolysis is promoted by conditions favourable to mildew growth.

— V. S. P.

SCREW DRUMS IN SOVIET TANNERIES AND POSSIBILITIES OF THEIR APPLICATION IN CZECHOSLOVAKIA. Miroslav Spička (*Leather and Allied Trades Research Institute, Gottwaldov, Czech.*) *Kožarstvi* 7, 68-70 (1957); *Chem. Abstr.* 52, 15941 (1958). This apparatus consists of a very long (16 to 30 m) horizontal cylinder about 2.5 m. in diameter, divided into compartments by a helical partition. Skins and liquor enter the first compartment. Agitation is effected by a rocking motion through 170-220°. At suitable intervals, skins are advanced to the next compartment by turning the drum through 360°. Details are given for using this type of apparatus for soaking and liming and for vegetable tanning. Advantages claimed are reduced floor space and increased productivity owing to decreased manual handling.

BUILDING AND LOCATION OF TANNERIES. Liboslav Masner (*Leather and Allied Trades Research Inst., Gottwaldov, Czech.*) *Kožarstvi* 7, 20-2 (1957); *Chem. Abstr.* 52, 15941 (1958). Data are given on capacities of new U.S.S.R. and Czech tanneries. About half the hand labour in older tanneries is internal transport, which can be eliminated by mechanization (see preceding abstract). The output of a new Czech tannery, in hides per worker per week, is stated to exceed that of specified U.S.A. tanneries by factors varying from 1.25 to 2. Concrete tan pits should be protected by ceramic tile. Painting with alcoholic PhOH-HCHO resins gave poor results. Lining the pits with poly (vinyl chloride) is unsuitable if temperatures > 45° are encountered. Tannery sewage can be discharged to a stream, after removal of 80-90% of suspended solids by sedimentation, if a minimum dilution of 200 : 1 is available on at least 350 days per year; otherwise chemical or biological purification is necessary. Cold, sterile well water is preferred for soaking and liming; a filtered, soft water is best for other purposes. Water consumption is 4000% of fresh hide weight for sole leather tanneries and 8000% for upper leather tanneries.

NOTES & NEWS

UPPER LEATHER IMPORTS (INTO U.K.) AT THE END OF AUGUST 1958

3,000,415 sq. ft. of full chrome calf and hide upper leather were imported into U.K. during August 1958, bringing the total for the first eight months of the year to 28,403,935 sq. ft. Commonwealth countries have sent 64.2 per cent of this total, with Australia sending 55% of the Commonwealth total.

Leading importers of box and willow calf are France and India. Over a million square feet of other chrome hide uppers have come from both India and Uruguay.

The imports (in sq. ft.) from India for the period Jan.-Aug. 1958 are: Box and willow calf: 2,075,312; Box and willow sides: 1,612,211; other chrome hide uppers: 1,942,812. Total full chrome calf and hide upper: 5,630,335; Glace kid: 175,404; Suede kid: 271.

Leather Trades' Review: 5-11-1958.

LEATHER AS A LIFE SAVER

Leather plays a vital part in the functioning of iron lungs in hospital and also in the rapid inflation of rubber rafts needed for air and sea rescue work.

Though bellows are no longer used extensively in blacksmiths' shops, their application has been rapidly extended to providing air pressure for foundry moulders, inflatable huts for troops, respiratory equipment for oil tanker inspectors and dock divers examining hulls of ships in port, brazing apparatus for technical colleges and schools, and iron lungs in hospitals. Other bellows have been specially designed to blow up toy balloons; there are small hand bellows for spraying chemical powders.

Only vegetable tanned leather of good quality, probably first selection, about 1¼ to 1¾ mm thick, and free of warble holes, cuts and splits is used. Split hide leathers are best suited to the manufacture of bellows, especially larger foot operated bellows. Coloured skiver leathers are used for fancy bellows and E. I. sheep

and russet hide leathers go into the production of some of the lighter, hand operated bellows such as one used for inflating rubber rafts.

After cutting, the leather is dipped into a specially, prepared bellows oil which has a high mineral content, to enhance the friction resisting properties of leather. Then the leather is piled, allowed to drip-dry, the oil penetrating the leather evenly immediately on contact.

Leather Trades' Review : 8-10-1958.

AUGUST EXPORTS OF INDIAN GOATSKINS FROM CALCUTTA

During August approximately 360,000 pieces of Indian goatskins were exported from Calcutta, compared with about 1,292,000 for the same period last year, comprising :

Drysalted : About 256,000 all of which were for the U.K. and the Continent.

Wetsalted : About 98,000 of which about 57,000 were for the U.K. and the Continent, and about 41,000 to the U.S.A.

Kidskins : About 6,000 to the Continent.

Of the total shipped about 163,000 pieces were for the "Iron Curtain" countries.

Leather Trades' Review : 8-10-1958.

INDIAN GOATSKIN EXPORTS FROM CALCUTTA IN SEPTEMBER

During September, approximately 311,000 pieces of Indian goatskins were exported from Calcutta, compared with about 527,000 for the same period last year, comprising:

Drysalted : About 186,000 of which 159,000 were for the U.K. and the Continent, and about 27,000 to the U.S.A.

Wetsalted : About 113,000 of which about 51,000 were for the U.K. and the Continent, and about 62,000 to the U.S.A.

Kidskins : About 12,000 to the Continent.

Of the total shipped, about 74,000 were for the Iron Curtain countries.

Leather Trades' Review : 5-11-1958.

NEW UNHAIRING PROCESS

New method of removing hair from animal hides is under development by the U.S. Department of Agriculture, reports the Financial Times. This method, it says, may permit packers to unhair hides themselves, cutting the cost of shipping hides to tanneries and allowing more accurate hide grading.

With the new method, the hair is loosened sufficiently for removal by soaking the hide in an enzyme solution for about 24 hours after pretreating it two or three days in a solution containing 26% salt.

The treatment seems to affect the basement membrane, a layer just below the hide surface that helps to anchor the animal hair. Salt treatment alters the nature of this membrane, and the enzyme solution then removes it almost entirely.

Leather Trades' Review : 29-10-1958.

NEW UNTANNED LEATHER, EXTREMELY LIGHT AND DURABLE

A patent has been granted to the Leather Industries Research Institute of Grahamstown, South Africa, on a new low density leather said to be four times lighter than water; with this leather shoes will be one-quarter of their present weight. The leather achieves its lightweight properties through the elimination of the tanning process. By treating the open fibre leather with silicone oil or synthetic resins it is made waterproof. Test shoes soled with this low density leather are said to have shown exceptional durability.

Leather Manufacturer, 75, No. 10, 26 (1958).

USDA RECOMMENDS INSECTICIDE TO CONTROL LIVESTOCK PESTS

The U.S. Department of Agriculture now recommends the use of Bayer 21/199, 0-(3 chloro-4-methyl umbelliferone) 0,0-Diethylphosphorothioate, commercially available as CO-RAL. It may be used with proper precautions on beef cattle for control of cattle grub, horn flies, lice, sticks, reds and screwworms. 21/199 should not be applied to sick animals or calves less than 3 months of age. It is not recommended for use on dairy cattle or milk goats, since it is known to secrete in the milk for a week or 10 days following treatment. When applied externally as a

spray, Bayer 21/199 is absorbed and kills 75-100 per cent of young cattle grubs.

Leather Manufacturer, 75, No. 9, 19 (1958).

LARGEST FOOTWEAR COLLECTION IN EUROPE TO BE SHOWN AT HARROGATE, ENGLAND

Britain is the top exporter of footwear in the world, and it is therefore fitting that the biggest shoe exhibition ever to be held in Europe will take place at Harrogate, England on April 7, 8 and 9th, 1959. Here will be provided a first class opportunity for discriminating buyers to see what shoes will be worn in many parts of the world next Autumn.

Harrogate, situated in the middle of England, is ideally suited for such an exhibition as it is easily accessible from both London and the Coast by road and rail.

The Majestic Hotel—one of the largest luxury hotels in the North of England—has been taken over for the purpose.

As a result of the success of the Exhibition last year when it was held for the first time, its size has increased by 100%, and over 160 individual showrooms will be exhibiting all that is new in British footwear for the Autumn. Manufacturers who are showing are responsible for the production of over 60 million pairs of shoes per year.

One of the highlights of this Footwear Exhibition will be fashion shows staged twice a day where the buyer will see all that is new in British fashion.

Social functions have also been organised and will include a Federation dinner and dance, cocktail party and a Civic Reception by the Mayor and Mayoress of Harrogate.

All enquiries regarding travel and hotel facilities should be addressed to the British Footwear Manufacturers Federation at 22, Gilbert Street, London, W. 1.

PETROLEUM FUELS AND SOLVENTS-BURNING QUALITY AND WICK-CHAR

Petroleum products such as fuels, lubricants, waxes and solvents occupy a key position in the industrial development of a country. In India, the production of petroleum products is being increased at an accelerated pace. In order to meet the needs of

this industry, and with a view to have standard methods of sampling and test, the ISI has drafted an Indian Standard Method of Test for Petroleum Fuels and Solvents-Burning Quality and Wick-Char [Doc : CDC 22 (781)].

The standard lays down three methods for evaluating the burning qualities of petroleum fuels and solvents, depending upon the quality of the material to be tested, namely, Method A for kerosene oil that may be used as an illuminant and as a fuel for space heaters, cookers, incubators, etc.; Method B for kerosene oil used for long time burning such as in railways semaphore signal lamps; Method C for special illuminating oils generally known as mineral seal oil or mineral colze oil used in railway coach lamps.

The methods included in the draft standard are based primarily upon the standards issued by the Institute of Petroleum, London, and American Society for Testing Materials, U.S.A., which have the wider acceptance all over the world in the petroleum industry. It was also felt that this would facilitate adoption of International Recommendations that may emerge out of the deliberations of the Technical Committee on Petroleum Products of the International Organization for Standardization (ISO/TC 28).

Copies are available, free on request, from the offices of the Indian Standards Institution, New Delhi, Bombay, Calcutta and Madras.

SPECIFICATION FOR MACHINERY AND SPINDLE OILS

The Indian Standards Institution has published an Indian Standard Specification for Machinery and Spindle Oils (IS : 493-1958). This standard was published in 1954, in which requirements for setting point had been prescribed. The setting point method has now become obsolete and has been replaced by the pour point method in the UK, USA and other countries. In order to fall in line with the international practice, the present version of the standard is being issued incorporating the changes suggested in the Amendment No. 1 to IS : 493-1954, published in June 1958.

This standard prescribes the requirements and the methods of test for machinery and spindle oils for various types of lubricating services to which these oils are employed. It does not cover oils compounded with fixed oils or soaps.

Copies of the standard, published in English and priced at Re. 1-00, are available from the offices of the Indian Standards Institution, at New Delhi, Bombay, Calcutta and Madras.

COAL TAR SOLVENT NAPHTHA, LIGHT

The Indian Standards Institution has published an Indian Standard Specification for Coal Tar Solvent Naphtha, Light, Grade 2 (IS : 1272-1958), which prescribes the requirements and methods of test for the material commercially known as coal tar solvent naphtha, light, grade 2.

A good proportion of the indigenous production of coal tar solvent naphtha, light, fails to meet the requirements of IS: 213-1956 Coal Tar Solvent Naphtha, Light, Grade 1, but is nevertheless, of use in some industries. In view of this, the Institution has sponsored the formulation of the standard. It is, however, expected that the entire indigenous production will improve in quality in the course of the next five years when this standard and also IS : 213-1956 may require review and revision. This specification is one of a series of Indian Standards on materials produced by the carbonization of coal. Other Indian Standard Specifications published so far in the series are :

- IS : 213-1956 Coal Tar Solvent Naphtha, Light, Grade 1
- IS : 214-1956 Coal Tar Solvent Naphtha, Heavy
- IS : 358-1953 Benzole, Industrial, Grade 2
- IS : 359-1953 Xylole, Industrial Solvent Grade
- IS : 534-1955 Benzene, Ordinary
- IS : 535-1955 Benzene, Pure, Nitration Grade.

Copies of the standard, published in English and priced at Rs. 1.50, are available from the offices of the Indian Standards Institution, located at New Delhi, Bombay, Calcutta and Madras.

INDIAN STANDARDS CONVENTION—1958

The Indian Standards Convention 1958 was held at New Delhi from 24th to 29th November, 1958, with six technical sessions. The following papers were presented at the Convention, from the Central Leather Research Institute :

1. Necessity of standardisation of cured skins for export promotion — S. N. Sen and S. C. Nandy.
2. A Study of some quality factors for the promotion of export of tannery wool and hair — S. K. Barat.
3. Standardisation and quality control within the small and cottage scale sectors of the Indian Leather Industry — S. K. Barat.

The first two papers were presented in the session S4 : Standardisation and Export Promotion and the third in session S6 : Sampling for quality evaluation.

SHANTI SWARUP BHATNAGAR MEMORIAL TOURNAMENT, 1958-1959

The Shanti Swarup Bhatnagar Memorial Tournaments were held at Madras from 24th to 31st December, 1958. These are held every year, with the Clubs of the various Institutes under the Council of Scientific & Industrial Research participating in them. This year, sixteen Institutes' Clubs entered the Tournaments. The Central Leather Research Institute Club was the Host Club.

The Tournaments were inaugurated on the 24th December, 1958, by Shri M. Bhakthavatsalam, Minister for Home Affairs, Madras State, who also hoisted the CSIR Club flag. The Tournaments concluded on the 31st December, 1958. The Prize Distribution ceremony was held on the same day with Dr. A. Lakshmanaswamy Mudaliar, Vice-Chancellor, University of Madras, and Chairman, Executive Council, Central Leather Research Institute, presiding; Prof. M. S. Thacker, Director-General, Scientific & Industrial Research and Secretary, Ministry of Scientific Research & Cultural Affairs, gave away the prizes. The winners of the various events are given below :

1. CRICKET:

Winners : National Chemical Laboratory Club, Poona.
Runners-up : National Physical Laboratory Club, New Delhi.

2. TENNIS :

Winners : National Metallurgical Laboratory Club, Jamshedpur.
Runners-up : National Physical Laboratory Club, New Delhi.

3. TABLE TENNIS :

Winners : Central Fuel Research Institute Club, Jealgora.
Runners-up : Central Food Technological Research Institute Club, Mysore.
Third place : Central Leather Research Institute Club, Madras.

4. BADMINTON (SHUTTLE) :

Winners : National Physical Laboratory Club, New Delhi.

Runners-up: Council of Scientific & Industrial Research Club, New Delhi.

Third place: Central Building Research Institute Club, Roorkee.

5. VOLLEY BALL:

Winners: National Botanical Gardens Club, Lucknow.

Runners-up: Central Road Research Institute Club, New Delhi.

Third place: Central Drug Research Institute Club, Lucknow.

6. FESTIVAL CRICKET:

Winners: Shri P. M. Sundaram (Secretary's) XII.

Runners-up: Prof. M. S. Thacker (Director-General's) XII.

7. TUG-OF-WAR:

Winners: Team composed of the Managers of the CSRI, CFRI, CFTRI, CRRI, CLRI, CSIR, NBG., & NML. teams.

Runners-up: Team composed of the Managers of the CMRS, CDRI, CBRI, CECRI, CEERI, RRL, NPL & NCL teams.

RESEARCH BEARS FRUIT

Practical Demonstration No. 1

(Third Series)

Process: Finishing of Chrome/vegetable tanned splits for fancy leathers.

Period: 27th January to 9th February, 1959.

Place: Central Leather Research Institute, Madras-20.

A process for the finishing of chrome/vegetable tanned splits for fancy leathers has been worked out at this Institute. It is proposed to demonstrate this process as the first in the third series of Practical Demonstrations from 27th January to 9th February, 1959.

If you are interested in this line of work, you are most welcome to send your representative/s to get trained in the manufacture of this type of leathers. You may kindly intimate the name/s of the representative/s who is/are likely to attend this demonstration. After following the process, we would request you to try this process in your Tannery and give us your valuable comments.

RESEARCH BEARS FRUIT

Practical Demonstration No. 2

(Third Series)

Process: Finishing of Chrome/vegetable tanned splits for fancy leathers.

Period: Starting from 19th February, 1959.

Place: Central Leather Research Institute, Madras-20.

A process for the Fancy finishing of E.I. tanned kips and skins has been worked out at this Institute. It is proposed to demonstrate this process as the next in the third series of Practical Demonstrations from 19th February, 1959.

If you are interested in this line of work, you are most welcome to send your representative/s to get trained in the manufacture of this type of leathers. You may kindly intimate the name/s of the representative/s who is/are likely to attend this demonstration. After following the process, we would request you to try this process in your Tannery and give us your valuable comments.

Programme (March-Aug.):

March: Retanning and finishing of clothing and jerkin leather from E.I. tanned skins.

April: Manufacture of Kattai and Banwar leather from Buffalo calf.

May: An improved method in chrome upper leather manufacture.

June: Manufacture of crushed and shrunken grain kid.

July: Manufacture of Football leather in plain and coloured finish.

August: Manufacture of chamois leather from Indian fish oil and C.L.R.I. sulphonated oil.

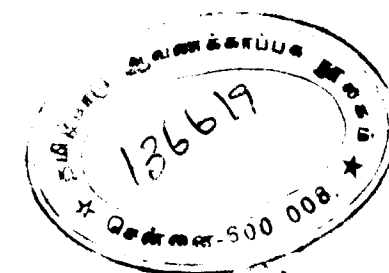
C. L. R. I. NEWS

The symposium on 'Tanning as a small-scale & cottage-scale Industry' will be inaugurated on the 15th February, 1959. The Technical Sessions will be held on the 16th and 17th February, 1959.

Dr. Y. Nayudamma, Director, attended the first meeting of the panel for leather and leather goods industries, constituted by the Ministry of Commerce & Industry, held at Delhi, on the 8th and 9th December, 1958.

Shri A. Ganesan, Senior Scientific Officer (Liaison), toured the Rajasthan and Madhya Pradesh States in connection with the organisation of extension service work.

Shri M. Thiruvengadam, Electrical-cum-Mechanical Engineer, Central Electronics Engineering Research Institute, Pilani, has been transferred to the Central Leather Research Institute.



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CLRI Publications

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PROCESS BULLETIN No. 2: Processes for the manufacture of Glazed kid. Re. 1/- per copy. Postage extra.

PROCESS BULLETIN No. 3: Manufacture of Roller skis
Re. 1/- per copy. Postage extra.

PROCESS BULLETIN No. 4: Fish oil of the West Coast for the Indian Leather Industry. Re. 1/- per copy. Postage extra.

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