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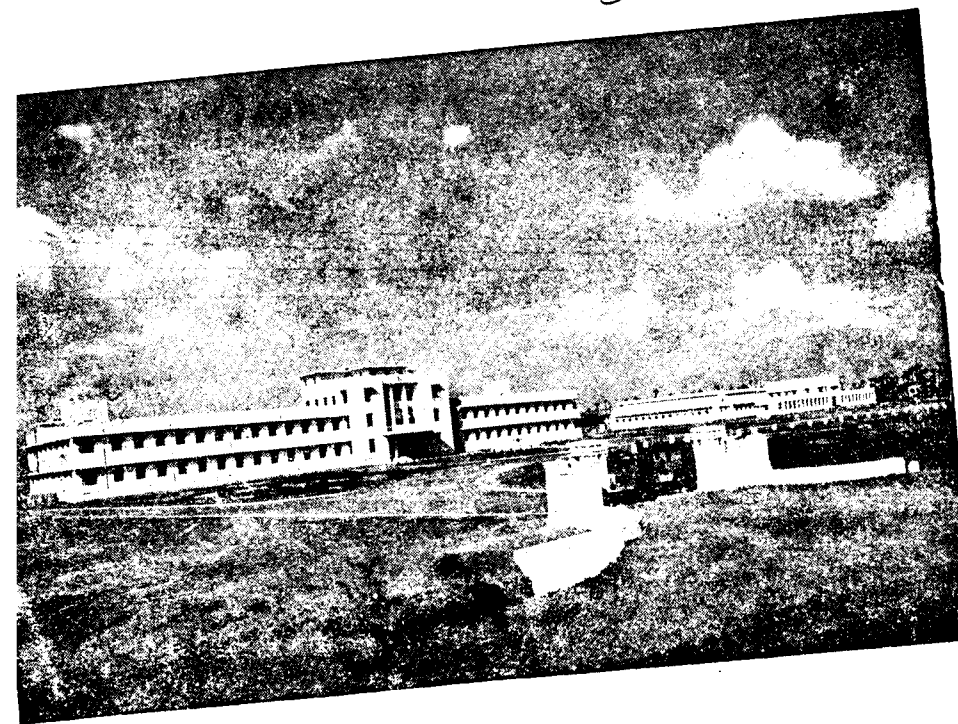


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STUDIES ON THE FORMATION OF MANNICH LINKAGES INVOLVING PHENOLIC COMPOUNDS WITH REFERENCE TO THE INTERACTION OF COLLAGEN WITH CERTAIN TANNING AGENTS

BY

S. RANGANATHAN, S. M. BOSE, & Y. NAYUDAMMA,

Central Leather Research Institute, Madras

Received on 11-8-1958

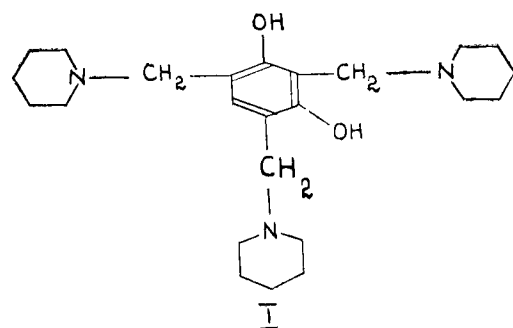
SUMMARY

Resorcinol has been shown to be capable of forming tris Mannich bases. Some evidence for the hypothesis that Mannich linkages are formed on retannage of vegetable tanned leather with formaldehyde is presented.

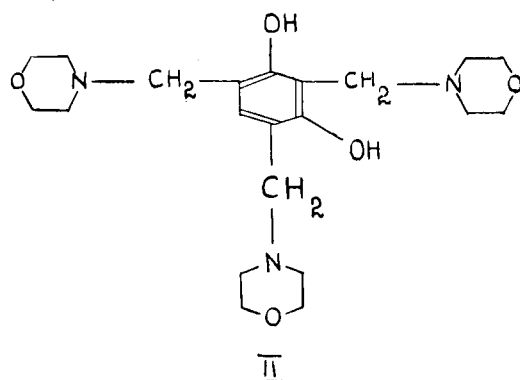
In the previous communications¹ dealing with tanning using resorcinol and formaldehyde, a mechanism involving the formation of C-Mannich linkages has been proposed. These linkages are believed to be responsible for the high hydrothermal stability of the leathers produced by such tannage. Indeed a study of this reaction on a quantitative basis has shown¹ that during the tanning, resorcinol and formaldehyde combine predominantly with the ϵ -amino groups of lysine, thus supporting the above view.

However, a survey of literature shows that no Mannich base involving resorcinol has been prepared; in addition it has been reported that an attempt to prepare the dimethyl amine Mannich base of resorcinol met with no success due to the formation of polymers. In view of this observation, it was felt very desirable to show that resorcinol was capable of entering into Mannich reaction.

In our hands too the reaction of resorcinol and formaldehyde with aliphatic amines resulted only in the production of polymeric material. However, the tris Mannich bases (I & II) involving resorcinol, formaldehyde and piperidine



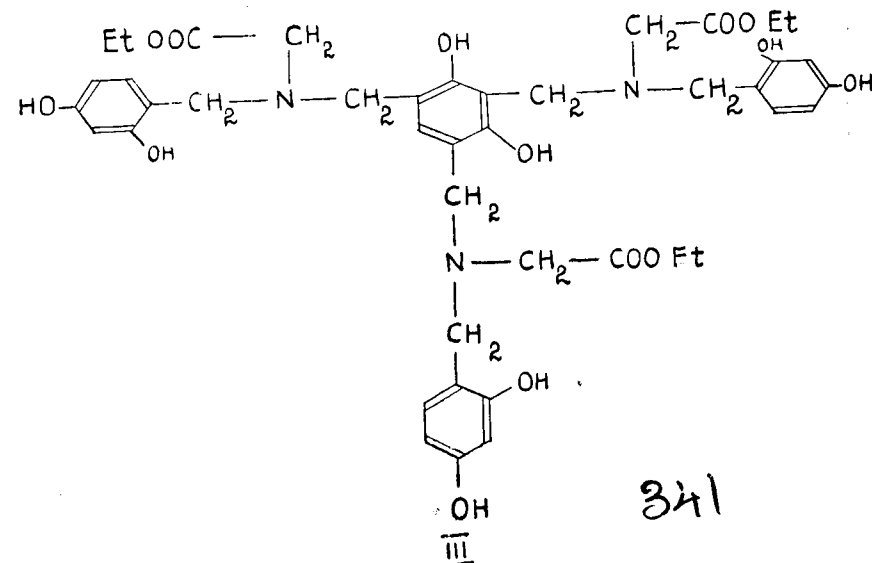
or morpholine have been successfully isolated under critical reaction conditions in low yields.



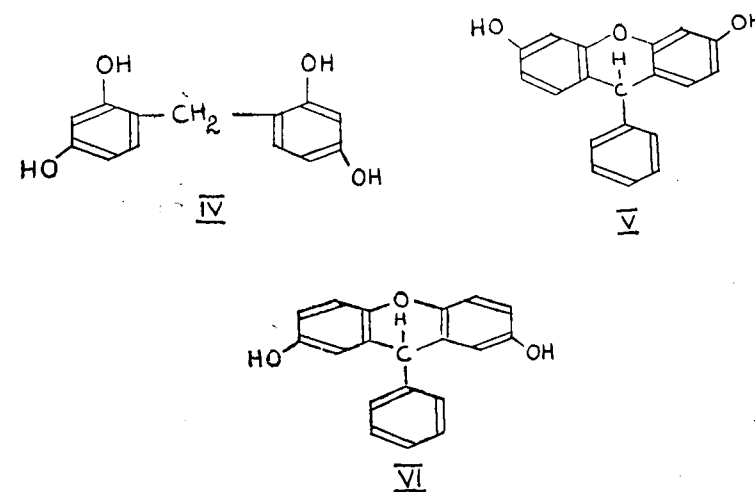
The reaction of glycine ethyl ester with resorcinol and formaldehyde provides material, which on the basis of analytical values could have formula III.

It is well known that the thermal stability of certain vegetable tanned leathers is increased considerably when retanned with formaldehyde.^{3, 4} It has also been found that all the formaldehyde bound could not be recovered from the retanned material.³ This may be due to the formation of C-Mannich base linkages which could be formed⁴ during the course of retanning. It was, therefore, deemed of interest

to make a study of the above reaction to find out whether any evidence could be obtained for or against the above hypothesis.

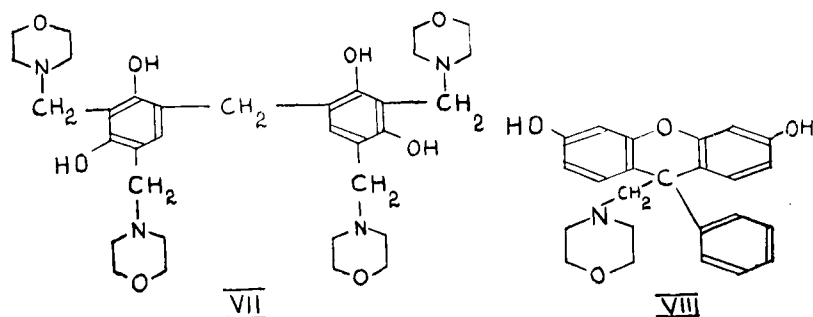


For this purpose bis(resorcy) methane (IV),⁵ 3, 7-dihydroxy-10-phenyl xanthene (V)⁶ and 2, 8-dihydroxy-10-phenyl xanthene (VI)⁶ were prepared and allowed to react



with pelt or collagen in aqueous methanolic medium both in the absence and presence of hexamethylene tetramine.

The amount of hexamethylene tetramine cleaved was determined and served as an indication to some chemical reaction taking place. Further to show that these compounds are sufficiently reactive to form Mannich bases, they were treated with morpholine and formaldehyde. The results indicate that the compounds IV and V probably form the Mannich bases VII and VIII respectively.



Experimental

2, 4, 6—tris (piperidino methyl) resorcinol (I):

5 ml. formalin (33%) was added to a solution of 4 ml. piperidine in 5 ml. water cooled in crushed ice and salt. The addition of formaldehyde was followed by that of an aqueous solution of resorcinol (5.5 g. in 8 ml.) at such a rate that the inside temperature did not rise above 0°C. A gummy mass separated immediately. The pH of the solution was brought down from 9.6 to 5.5 by careful addition of 5% acetic acid when the pasty material solidified after repeated rubbing (yield: 1.1 g., 16%). The crude material was crystallised from ethanol (mp. 148-149°C).

Calculated for $C_{24}H_{39}N_3O_2$: C 71.8; H 9.7; N 10.5

Found: C 71.3; H 9.5; N 10.8.

2, 4, 6—tris (morpholino methyl) resorcinol (II):

1 ml. formalin (33%) was added to a solution of 1 ml. morpholine in 5 ml. water cooled in crushed ice and salt. An aqueous solution of resorcinol (1.1 g. in 2 ml.) was

slowly maintaining the inside temperature below 5°C. The gummy mass separated was washed with water, extracted with ether when the product solidified to a powdery material. (yield: 150 mg.; 12%). The product was crystallised from ethanol m.p. 206-207°C.

Calculated for $C_{21}H_{33}N_3O_5$: C 61.9; H 8.1; N 10.5

Found: C 62.7; H 8.3; N 10.2.

Reaction of glycine ethyl ester hydrochloride with resorcinol and formaldehyde.

Glycine ethyl ester hydrochloride was prepared as recommended by Marvel.⁷

1 ml. formalin was added to an aqueous solution of glycine ethyl ester hydrochloride (1.4 g. in 10 ml.) cooled in ice and salt. An aqueous solution of resorcinol (1.1 g. in 2 ml.) was then added slowly and the mixture warmed up. After the completion of the reaction the pH of the solution was slowly brought from 3.1 to 5.0 by very careful addition of 10% sodium hydroxide solution. The gummy material which separated solidified on repeated trituration with water (yield 1 g.).

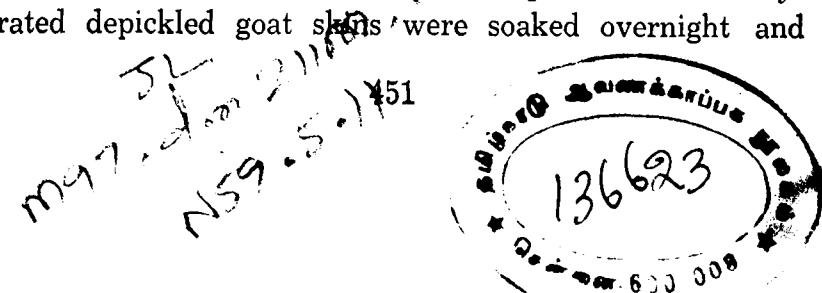
For analysis the material was purified by dissolution in dilute acetic acid and by reprecipitation using sodium bicarbonate solution (mp. 118-120°C).

Calculated for $C_{42}H_{51}N_3O_{14}$: C 61.5; H 6.2; N 5.1

Found: C 60.7; H 6.2; N 5.0.

Tanning experiments with (a) Bis(resorcyl)methane, (b) 3, 7-dihydroxy-10-phenyl xanthene and (c) with 2, 8-dihydroxy-10-phenyl xanthene both in presence and absence of hexamethylene tetramine. (HT).

Compounds IV, V and VI were prepared according to methods reported in literature.⁸ Strips of acetone dehydrated depickled goat skins were soaked overnight and



weighed. A weighed piece of the skin was introduced into an aqueous methanolic solution of the model compound (10% on the pelt weight) and hexamethylene tetramine (equimolecular amount corresponding to the model compound taken) and the mixture allowed to stand at room temperature for a period of 40 hours with intermittent shaking. The blank experiments were carried out in identical manner without the addition of hexamethylene tetramine. The blank and the experiment were done with portions of the skin taken from the same location. After tanning, the pieces were washed, dried and their shrinkage temperatures determined. These are presented in Table I.

TABLE I

Compound	Shrinkage Temperature °C	
	Without HT	With HT
	.. 60	—
Bis (resorcy) methane	.. 84	104
3, 7-dihydroxy—10-phenyl xanthene	.. 75	80
2, 8-dihydroxy—10-phenyl xanthene	.. 67	68

Interaction of the model compounds and hexamethylene tetramine with collagen and their stability in aqueous methanolic medium.

A solution prepared from 100 mg. of hexamethylene tetramine and 100 mg. of the model compound in excess 90% methanol was allowed to react at room temperature with 1 g. of collagen for 40 hours. A blank was simultaneously run without collagen. After reaction the collagen was repeatedly washed with water, the residual liquor and the total washed water were made up to a suitable volume

and the amount of unreacted hexamethylene tetramine was estimated. An aliquot of the made up solution was heated for 30 minutes with *N*/10 sulphuric acid, cooled, and then neutralised carefully by addition of standard NaOH. The neutralised solution was treated with excess potassium bisulphite and the unused potassium bisulphite was estimated by titrating against standard iodine solution.⁸ The amount of unused hexamethylene tetramine was calculated from the amount of formaldehyde found. The unreacted hexamethylene tetramine in the blank solution was also determined by employing the same method. The results are presented in Table II.

TABLE II

Name of Compound	Amount of H.T. unused in mg.	
	Blank	Collagen
Bis (resorcy) methane	.. 97.7	89.2
3, 7-dihydroxy—10-phenyl xanthene	.. 98.3	93.4
2, 8-dihydroxy—10-phenyl xanthene	.. 98.7	98.1

Interaction of model compounds with morpholine and formaldehyde.

Equimolecular amounts of the model compounds, morpholine and formaldehyde in excess methanol were mixed. In the case of bis(resorcy) methane and 3, 7-dihydroxy-10-phenyl xanthene there was an immediate exothermic reaction and a compound was thrown out of solution. But in the case of 2, 8-dihydroxy-10-phenyl xanthene there was no reaction. The precipitates formed were powdery and were not soluble in organic solvents. For analysis they were

repeatedly washed with water and ethanol and dried. The results are given in Table III.

TABLE III

Compound		M.P.	Analytical values		
		°C	C	H	N
Product from Bis (resorcyl) methane (a)	..	300	59.8	6.2	8.7
Product from 3, 7-dihydroxy 10-phenyl xanthene (b)	..	230	72.9	5.8	3.5

(a) Calculated for formula VII— $C_{33}H_{48}N_4O_8$:—
C 63.05; H 7.6; N 8.9.

(b) Calculated for formula VIII— $C_{24}H_{23}NO_4$:—
C 74.0; H 5.9; N 3.6.

Discussion

It is not surprising that previous attempts to make Mannich bases involving resorcinol did not meet with success since the great reactivity of the resorcinol nucleus makes the conditions of the reaction very critical. It has been observed that even slight variation of experimental conditions will cause failure in isolation of any crystalline material. Several attempts were made without success, to find out if any product other than the tris Mannich bases is formed in the course of the reaction. It was found absolutely essential to keep the temperature at or below 0°C since even at fairly low temperatures the reaction proceeded violently with the production of polymeric material. Here again resorcinol offers a sharp contrast to phenol. While the latter produces the tris Mannich bases only at 95°C⁹ resorcinol yields the tris bases at low temperatures.

It will be interesting to speculate at this juncture as to how the results obtained fit in with the theory of formation

of Mannich linkages in tanning with resorcinol and formaldehyde. It has to be emphasized that while the above mentioned reactions occurred in a homogeneous system, tanning occurs in a two phase system and so the reaction is well controlled. So, it will not be too unreasonable to suppose that there are greater possibilities for the formation of more Mannich linkages during tanning than in reactions involving a single phase system, since in the former case the formation of polymers involving the amino groups may not be possible.

The fact that tris Mannich bases are formed shows that resorcinol is capable of being used as an active centre for multipoint fixation. Only such fixation can explain the high thermal stability of the tanned material. In the case of glycine ethyl ester, the expected product was not obtained. However, the compound obtained could have formula III on the basis of carbon, hydrogen and nitrogen analysis.

Tu and Lollar⁶ had tested the tanning potentials of a variety of phenolic compounds in the hope that information might be obtained concerning the requirements for a phenolic compound to have good tanning properties. Their comprehensive study brought out the fact that even the position of the hydroxyl groups determined the tanning potential of a compound. For example, they found that while 3, 7-dihydroxy-10-phenyl xanthene had good tanning action, the isomer 2, 8-dihydroxy-10-phenyl xanthene had no tanning properties. This was argued to be due to the fact that with the hydroxyl group in the *para* position with respect to the methylene bridge, the activity of the molecule was considerably increased. From the foregoing discussion it has been brought out that for the formation of Mannich linkages during tanning, the tanning agent should have pronounced activity. A comparison of data obtained with IV, V and VI clearly shows that in cases where the compound possesses good tanning properties, treatment with

hexamethylene tetramine increases the thermal stability and this is probably due to the cleavage of hexamethylene tetramine to ammonia and formaldehyde and the subsequent reaction of the compound and formaldehyde with the protein, forming Mannich linkages.

This view is further supported by the fact that IV and V readily react with morpholine and formaldehyde to yield probably the Mannich bases VII and VIII respectively.

The fact that probably VIII is formed on treatment of V with morpholine and formaldehyde indicates that V is sufficiently reactive to produce only mono Mannich bases unlike resorcinol and this explains the small rise in thermal stability.

As could be expected, IV is a very reactive compound and reacts with pelt with ease and this is indicated by the increase in shrinkage temperature by tanning with this compound. The fact that on tanning with IV and hexamine the shrinkage temperature rises to 104°C and the fact that a good amount of hexamethylene tetramine is cleaved during the reaction shows that the compound provides itself as a site for multipoint fixation as postulated by Windus.⁴

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RESEARCH BEARS FRUIT

Practical Demonstration No. 6

(Third Series)

Pretreatment with Calgon (Phosphate Glass 696) for Chrome Tanning of Upper Leather*

S. P. GHOSE, S. N. BOSE & K. T. SARKAR

Introduction

Unlike vegetable tannins and basic chromium or aluminium sulphate, polymeric phosphates are not known to have been used successfully as the tanning agent for any kind of commercial leather. However it has been known for many years that polymeric phosphates coagulate protein and like most tanning actions, the vigour of the combination of the phosphate with protein is dependent upon the pH value. Calgon is a water soluble glass, developed as a water conditioner and is known to chemists, as polymeric sodium metaphosphate. Although, not known to have been used singly as tanning agent commercially, it has been found to have distinct advantages, as a pretanning material for chrome and vegetable tanned leather. Used in pretannage, calgon improves the fullness of the flanks, smoothness and tightness of the grain, consequently increasing the cutting value of the finished chrome upper leather. Calgon is available under the trade name "Phosphate glass 696" manufactured by Messrs Albright & Wilson Ltd, London (local agents Messrs. Imperial Chemical Industries India Private Ltd.). The following process has given very satisfactory

* Processes demonstrated in May 1959.

results and has been tried out at this Institute on a large scale.

Raw material: Wet salted cow hides weighing 14-17 lbs. each.

Soaking: The wet salted raw materials are soaked overnight in a pit or in a paddle containing 0.5% bleaching powder in 500% water (based on raw wet salted weight). Next morning the hides are raw-fleshed, washed until the wash liquor is clear and horsed up to drain for an hour. The soaked weight is now noted.

Lime painting: The soaked hides are then painted on the flesh side with paint of composition given below, folded along the backbone line and piled into a pile of not more than 25 hides.

1.7% sodium sulphide conc.	} on the soaked weight.
8% slaked lime.	
12-15% water.	

The hides are kept undisturbed in the pile for about 4 hours and are then straight entered into a lime pit.

Liming: The liquor in the lime pit is of the following composition:—

2% sodium sulphide conc.	} on the soaked weight.
400% water	

The hides are left in the lime pit overnight. Next day they are unhaired and put back in the same pit after the following have been added and the lime liquor thoroughly stirred.

2.5-3.0 oz. % soda ash	} on the soaked weight.
3% common salt	

The stock is hauled up and put back, at least twice during the day and left in the pit, overnight.

Washing: Next morning the stock is rinsed, fleshed and scudded. The weight of the fleshed pelt is now taken.

Deliming and bating: The stock is now delimed in a drum, with 1-1½% boric acid and 200% water (on the fleshed pelt weight), for 20 to 30 minutes and left, without movement, in the drum during the night.

Next morning, the drum is run for 10-15 minutes and the bath drained away. Bating is carried out with

150-200% water, 32°C	} on the pelt weight.
0.4% C.L.R.I. Bate No. 2	

Total period of bating is 30-35 minutes. The bath is drained away and the stock scudded and briefly rinsed.

Calgon pretreatment is carried out with the composition given below:—

80% water	} on the pelt weight.
3½% phosphate glass 696	
(previously dissolved in water, 1: 10)	

The stock is drummed for 30 minutes, with this bath.

A mixture of 1.5-1.7% sulphuric acid (1.8d) and 10% water (on the pelt weight) is then added in six equal instalments at intervals of 30 minutes. Total drumming should be at least for 8 hours after which the pH of the pickle bath should lie between 2.6 and 3.0.

Rinsing: The pickled stock is given a short rinsing.

Chrome Tanning: One bath chrome liquor equivalent to 4-6% sodium bichromate (calculated on the pelt weight) is taken for chrome tanning. Tanning is done in the following manner:—

The pickled pelts are taken in a drum with 80% water. The prepared chrome liquor of 33% basicity is then added in two instalments at an interval of 30 minutes. After the last feed the drum should continue to run for further 3 hours and allowed to rest during the night.

Next morning the drum is run for 30 minutes.

Basification: 0·2-0·3% soda ash, dissolved in 15 times the quantity of water, is slowly added during one hour and drumming continued for one more hour. The pH of the exhaust tanning bath should lie between 3·3-3·5. The tanned hides are then horsed up smooth, grain to grain, for one day.

Shaving: The leathers are then sammed and shaved to 1·4-1·5 mm. The shaved weight is noted.

Neutralisation: The shaved stock is first rinsed for half-an-hour and neutralised with:

200% water	} on shaved weight.
7·5 oz. % sodium sulphite	
1·5 oz. % sodium bisulphite	

Drumming is for 30-40 minutes and the stock is then rinsed again. The pH of the neutralised leathers should be about 5·5 at the surface and sink gradually to 4·6-4·8 in the interior.

Dyeing: The dyeing bath is as follows:—

200% water at 60°C	} on the shaved weight.
0·7% Naphthalene Leather	
Brown ADS or any acid	
dye of desired shade.	

The dye is first made into a paste with a little cold water and then dissolved by pouring into 40-50 times the quantity of boiling water. The dye solution is then added to the drum in portions.

Fat-liquoring:—After running the drum for 30-35 minutes, the fat-liquor consisting of the following, is added:—

1·2-1·5% sulphated pungam oil	} on shaved weight.
0·8-1·0% untreated fish oil	
0·2% soap.	

After drumming for 30-40 minutes, the exhaust bath is drained away.

Refat-liquoring:—is carried out in a fresh bath with,—
150% water 55°C,
0·7% fish oil, and
0·2% C.L.R.I. Cationic dispersing agent.

The drum is run for 30 minutes, the bath drained away and the stock horsed up.

Samming, setting, drying, saw dusting, staking and nailing are carried out as usual.

Clearing:—A solution containing 50 g. lactic acid/litre is rubbed on the grain side with a brush. After this has dried finishing is carried out.

Finishing:—Ground Coat A — Composition:

100-125 gms. pigment paste of suitable shade.
50 gms. 10% linseed mucilage.
40 gms. 10% casein.
10 gms. T.R.O.
water to make 1000 cc.

The above is applied once by brush or pad and dried.

Season B: Composition:

1000 cc. ground coat A.
20 gms. 10% casein.
12 cc. formaldehyde.

One pad or brush coat of the season is given and then allowed to dry.

Level Coat:—Composition:

600 cc. ground coat A.
400 cc. season coat C (composition given below).

One cross coat is sprayed and dried.

Season Coat C :—Composition :

75 gms. 10% Casein binder.

25 gms. Egg albumin.

5 gms. Glycerine.

25 cc. Formaldehyde.

Water to make 1000 cc.

One cross coat of the above is applied by spray.

Fixing Coat :—Composition :

325 cc. Formaldehyde.

655 cc. water.

20 cc. Acetic acid.

One cross coat of the above is applied.

Leathers are then dried, glazed, measured and hot-plated at 150°F.

TECHNICAL SEMINAR

Cationic Detergents *

S. R. PALIT

Cationic detergents possess the following characteristics :—Wetting and emulsifying power and consequently ability to lower surface tension, formation of liquid crystals, positive electrical charge, and very powerful solubilising and germicidal properties.

Solubilisation phenomena, with a number of cationic detergents of the quaternary ammonium (cetyl or lauryl, alkyl dimethyl ammonium) type have been studied. The process of solubilisation has been found to involve a number of phase transitions. Liquid crystalline phases invariably occur in systems which are close to the solubilisation maximum. These liquid crystalline systems possess some special properties. They are birefringent and show polarisation colours and interference patterns. They possess a very high temperature co-efficient of electrical conductivity and hence their use as liquid thermistors is suggested. Also they exhibit Winsor phenomenon, i.e., when placed in a D.C. electric field of about 20 to 40 volts/cm they become hazy, and on switching off the field they become clear again.

In the study of solubilisation phenomena, it was found that the organic solvents tried could be broadly separated into two groups: (1) those for which the ratio of lipophilic and hydrophilic affinities R , was greater than one and (2) those with R less than one. The maximum

* Condensed from the talk given by Prof. S. R. Palit, Indian Association for Cultivation of Sciences, Calcutta, on 4-5-1959.

solubilisation was achieved when R was ~ 1 . So by mixing together two systems, one of R value greater than one and another of R value less than one, solubilisation was greater. Similarly a mixture of detergents belonging to the two solubilisation types, also was found to lead to greater solubilisation. The solubilisation behaviour of the detergents systems could be more rapidly interpreted by means of complete phase diagrams for the ternary systems, oil — soap — water.

The results obtained are in general agreement with Winsor's theory of solubilisation.

V. S. P,

TECHNICAL SEMINAR

Nature of tannins and phenolic non-tans in Myrobalan
(*Terminalia Chebula*)*

BY

K. J. SCARIA

Summary

The nature of tannins and phenolic nontans in myrobalan has been investigated using three different techniques. Fractionation of these constituents was first carried out separately (i) by paper strip electrophoresis and (2) by two dimensional paper chromatography. A combination of electrophoresis and chromatography gave better separation than obtained by either of the two individually. The phenolic constituents in myrobalan were separated by a combination of electrophoresis in the first dimension in veronal buffer followed by ascending chromatography in the second dimension in butanol: acetic acid: water mixture (4:1:5). The tan and non-tan fractions were differentiated using hide powder. The petroleum ether precipitated portion of the ethyl acetate extract of myrobalan separated into ten different constituents of which seven were found to be tannins and the rest non-tans. The absorptions of all these ten fractions in the ultra-violet region were studied in water and also with the addition of borate buffer against borate buffer and observations were made regarding their different behaviour.

* Summary of the talk given on 8-5-1959.

TECHNICAL SEMINAR

A New Hide Preservative: Paludrine *

BY

S. C. NANDY

Summary

1-(p-chlorophenyl)-5-isopropyl biguanide-HCl (paludrine-proguanil hydrochloride) has been found to be a good bacteriostatic agent besides being an anti-malarial. Its application as a preservative has been tried out in the Leather Industry. The antiseptic value of paludrine has been tested *in vitro*, i.e., in laboratory scale experiments in curing hides and skins either in presence or absence of salt and during soaking of dry, drysalted and wet salted hides. The concentration of paludrine to be used and the hide-soak liquor ratio have been worked out.

* Summary of the talk given on 15-5-1959.

CLASSIFIED ABSTRACTS

PROCESSES PRIOR TO TANNING

ENZYMIC UNHAIRING MATERIAL. II. COMPARISON OF ENZYMIC PROCESS WITH LIMING. Kenjiro Kondo. *Hyogo Noka Daigaku Kenkyu Hokoku* 3, 12-14 (1957); *Chem. Abst.* 52, 19199 (1958). Unhairing was caused after 4 days both by Rinase and $\text{Ca}(\text{OH})_2$ treatment. In liming, the skin was swollen and collagen was more digested than elastin while in the Rinase process, the skin was in the fallen condition and elastin was more digested than collagen.

MICROBIAL AND OTHER ENZYMES AS DEPILATORY AGENTS. T. C. Cordon, H. W. Jones, I. D. Clarke, and J. Naghski (Eastern Regional Research Lab., Philadelphia, Pa.). *Appl. Microbiol.* 6, 293-7 (1958); *Chem. Abst.* 52, 18961 (1958). The value of common enzymes including microbial preparations in loosening the hair from soaked green salted steer hides was investigated and the depilatory activity of these enzyme preparations was compared with their proteolytic and amylolytic activity. Thirty-seven preparations were used in the experiments including 13 from bacterial cells, 14 from fungal cells, 1 from yeast cells, and 2 from unidentified microbial origin. The depilatory activity could not be correlated with the proteolytic or dextrinizing power as measured by hydrolysis of casein and starch.

VEGETABLE TANNING

TANNIN OF BROWN ALGA, SARGASSUM RINGGOLDIANUM. Chinkichi Ogino and Yasuhiko Taki. *J. Tokyo Univ. Fisheries* 43, 1-5 (1957) (in English); *Chem. Abst.* 52, 18668 (1958). Tannin isolated from *S. ringgoldianum* belongs to a catechol variety according to the classification of Freudenberg. Paper chromatography in $\text{BuOH-AcOH-1\% NaHSO}_3$ (4:1:5) gave 4 spots with some tailing.

TANNIN CONTENT OF COTINUS COGGYRIA AND RHUS TYPHINA. N.KH. Osmola. *Nauch, Trudy L'vov. Lesotekh. Inst.* 3, 249-53 (1957); *Referat. Zhur. Khim., Biol. Khim.* 1958,

Abstr. No. 11301, Chem. Abst. **52**, 18686 (1958). Leaves of *C. coggygia* contained 24.24% of tannin substances; *R. typhina* contained 20.74%.

BARK IV: COMPARISON OF LIGNIN BETWEEN BARK OF GYMNOSPERMOUS AND ANGIOSPERMOUS TREES. Katsumi Hata and Murao Sogo (Univ. Kagawa, Kagawa-ken). *Mokuzai Gakkaishi* **4**, 85-90 (1958) (in English); Chem. Abst. **52**, 19125 (1958). Inner bark (I), outer bark (II), and sapwood of gymnosperms (4 species) and angiosperms (4 species) were extracted with EtOH-C₆H₆ and hot water, and then oxidized with NaOH-PhNO₂. The oxidation products were examined by paper chromatography to determine the presence of syringic acid, protocatechualdehyde, vanillic acid, 5-formyl vanillic acid, p-hydroxybenzaldehyde, syringaldehyde, vanillin, acetoguaiacone, and p-hydroxyazobenzene. I and II lignins of the gymnosperms had the guaiacyl type (III), p-HOC₆H₄ type (IV), and 3, 4-(HO)₂C₆H₃ type (V) building units, and may or may not have a small amount of the syringyl type (VI) of building unit, whereas I and II lignins from angiosperms had III, IV, V, and VI. Fibrous tissues in I and II of the angiosperms gave the purple Maule test.

ESTIMATION OF THE TANNING VALUE OF THE SUMACS CULTIVATED IN POLAND. Regina Zielinska (Akad. Med., Lodz, Poland). *Dissertationes Pharm.* **9**, 35-41 (1957); Chem. Abst. **52**, 19202 (1958): The properties and tannin content of the leaves of *Rhus typhina* (26.92% tannin) and of *R. cotinus* (25.56% tannin) were investigated. Tannins were determined by the hide-powder method, the gravimetric Cu method, and the gravimetric-volumetric Cu-iodometric method. The tanning content increases with the development of the plant to a maximum in October.

PINUS RADIATA BARK TANNIN. H. E. Booth, W. J. Herzberg and F. R. Humphreys (Forestry Comm. N. S. W., Sydney), *Australian J. Sci.* **21**, 19-20 (1958); Chem. Abst. **52**, 19203 (1958). *P. radiata* bark ground to pass through a 44-mesh sieve and counter current extracted with water at room temperature gave a light-coloured extract substantially free from insolubles. An 8% solution spray dried readily to give a fawn powder soluble in cold water. The tannin reacted rapidly with HCHO even at room temperature. This reaction was used to make a hot-press plywood adhesive, a waterproof cold-setting adhesive, and an adhesive for hot-pressed chipboards.

CONDENSED TANNINS. I. A STUDY OF COMPLEX LEUCOANTHOCYANINS PRESENT IN CONDENSED TANNINS. D. G. Roux and S. R. Evelyn (Rhodes Univ., Grahamstown, S. Africa). *Biochem. J.* **69**, 530-8 (1958); Chem. Abst. **52**, 19201 (1958). Examination of the heartwood extractives of 144 "hardwood" species show that 33% give strongly positive reactions for leucoanthocyanins. Lower R_f polymeric forms predominate, and in only 12%, mainly among the *Leguminosae*, is evidence found of the presence of monomeric leucoanthocyanins. Black-wattle and quebracho tannins have been shown to be relatively rich in complex leucorobinetinidins and leucofisetinidins. Comparison of the yields of anthocyanins from complex naturally occurring leucoanthocyanins and from synthetic monomeric leucoanthocyanins indicates that about 25% of the "fundamental units present in these complex tannins are of the leuco-anthocyanin type. For each tannin mixture, a gradational increase of molecular weight with decrease of R_f value of the tannins was found, when separated on paper chromatograms in 2% AcOH. The molecular weights of wattle tannins fall mainly in the range 550-1630, although a small fraction of much higher molecular weight (3240) is also present. Values for quebracho tannins fall in the range 800-2350. Similar proportions of leuco-anthocyanins are present throughout the whole molecular weight range of both tannins, indicating the presence of leucoanthocyanins (e.g., leucorobinetinidins and leucofisetinidins) of increasing complexity from the higher R_f (0.5-0.6) to the lower R_f (0) regions. With increase in molecular weight condensed tannins show a parallel increase in "affinity" for cellulose, and also for collagen.

OTHER TANNAGES

SOLVENT TANNAGE (WITH SYNTANS). Hellmuth Weber (Zavody Ant. Zapotockeho, Hradek nad Nisou, Czech.). *Kožářství* **7**, 88-91 (1957); Chem. Abst. **52**, 19203 (1958). A new syntan made from 6 moles dihydroxybenzenes and 1 mole phenol, condensed with HCHO, and sulfonated with H₂SO₄, was soluble in water, but the viscosity was too high for use in tanning. Products called A-syntans (I), soluble in EtOH but insoluble in H₂O, have been prepared from dihydroxybenzenes. I is prepared by condensing "Difen" with HCHO by using H₂SO₄ as catalyst. Products with molecular weights of 574-1516 were prepared, of which the highest molecular weight was the best. This I contains about 15 pyrocatechol rings, 30% phenolic OH groups, and no SO₃H groups, and therefore resembles vegetable tannin. Its pH is about 4.5-5.0. By

addition of 10-15% EtOH a solution is obtained with about the same viscosity as a vegetable tannin extract. Solutions of *I* in EtOH have good tanning properties. Light skins are tanned in 3-5 hrs. and heavy hides in 24-60 hrs. Tannage is done in drums with 40% *I* and 100% EtOH on the hide weight. The spent liquor is treated with H₂O to precipitate excess *I*, which is recovered, and EtOH is recovered from the filtrate by distillation. Shrinkage temperatures from 90 to > 100° have been obtained. The leather shows a degree of tannage of 84%, practically no H₂O-soluble matter, and a yield value of 222. Pretannage with 0.6% Cr₂O₃ or lowering the pH during tannage to 3.8 produced no improvement.

AN ACID-CATALYZED POLYCONDENSATION OF o-DIHYDROXYBENZENE WITH FORMALDEHYDE. Zdenek Kotasek and Jaroslav Strachota (*Leather & Allied Trades Research Inst., Gottwaldov, Czech.*). *Věda a výzkum v průmyslu kožedělném* 3, 25-42 (1958); *Chem. Abst.* 52, 19200 (1958). The polycondensation of phenolic syntans has been studied. This work should form a theoretical basis for producing Syntan P2 with no-SO₃H groups from technical pyrocatechol (*I*) and HCHO with HCl catalyst. The condensation of *I* has been followed by paper chromatography. An apparatus is described for making several condensations at one time. Condensations were made at 60° to condensation degrees of 0.63, 0.70, and 0.77, by using 15.7 g. *I*, 6.57, 7.7, and 8.8 g. HCHO (39.2%), and 0.86 g. HCl (37%) in 31.0 g. H₂O. The products were analyzed for free *I* by ascending chromatography with CCl₄ and CHCl₃ (2:1), by using 3% phosphomolybdic acid in aqueous. EtOH and NH₃ vapor for development. The *I* content was determined with a densitometer. Condensation practically ceases after 6 hrs. The pilot plant P2 contained about 15% free *I*; laboratory preparations made with 0.55 and 0.70 moles HCHO contained 40.5 and 28.5% free *I*. Condensates of *I* have been fractionated by column chromatography on polycaprolactam and eluted with H₂O-saturated *tert.*-BuOH. Free *I* is preferentially absorbed. Column chromatography on a basic MDF Annex gives the same results and can be used commercially to free P₂ from *I*. A colorimetric method has been worked out for determining free *I* to within 3% with phosphomolybdic acid at pH 3.5.

INFLUENCE OF SYNTANS ON SLUDGE FORMATION IN TAN LIQUORS AND ON PHYSICAL PROPERTIES OF LEATHER. Rudolf Exner and Jaroslav Kabrt (*Zavody Ant. Zápotockeho, Hradec nad Nisoum Czech.*) *Věda a Výzkum v*

průmyslu kožedělném 3, 63-77 (1958); *Chem. Abst.* 52, 19203 (1958). Sludge (*I*) was measured in tan liquors, with and without added syntan (*II*), by using a more refined method than previously employed. Since *I* becomes irreversibly less colloidal on cooling, the tan liquors were diluted with water at 0°. The amount of *I* thus formed is larger but more reproducible. Co-efficient of variance of the determination of sludge is $\pm 19.7\%$ for most tannins ($\pm 12.4\%$ for wattle) compared to $\pm 45\%$ for insoluble matter determined by the filter method. Tannins studied were spruce bark, sulfited quebracho, sulfited oak wood, wattle, and chestnut extracts, and *II* used were SN₂₅, K₂D, Omega, Kortan Q₁, and Kortan QD. Stock Solutions were prepared containing 17-29% tannin, and 120 molecule portions were diluted to 1 l, with water at 1-2°C, stored overnight, and filtered. Binary tannin mixtures contained upto 50% more *I* than individual tannins. Addition of *II* to vegetable tan liquors lowered average *I* to 40 to 88% of the initial value, depending on the particular *II* employed. K₂D was much the most effective. Only K₂D and Kortan Q₁ lowered *I* in *III*, and only K₂D, Kortan Q₁, and sometime Omega lowered *I* in ternary tannin mixtures. For leathers tanned with blends containing 20, 32, and 50% *II* in the total tannin, tear resistance was lowest for 20% *II* and was the same for 32 and 50% *II*. Degree of tannage was lower for 50 than for 32% *II*. Water-soluble matter was minimum for 32% *II*. Leather tanned with sulfited *III* plus 30% *II* had a distinctly lower tear strength and contained 16% more soluble matter than did leather tanned with unsulfited *III* and 20% *II*. For leathers tanned with blends containing 50% *II*, sulfited *III* gave 11% lower tear strength, 13% higher degree of tannage, and 11% less soluble matter than unsulfited *III*.

SYNTANS USED BY THE POLISH LEATHER INDUSTRY. Edgar Bischoff (*Leather and Allied Trades Research Inst., Warsaw*). *Kožářství* 7, 46-9 (1957); *Chem. Abst.* 52, 19202 (1958). Polish syntans (Rotanins) correspond to the I.G. syntans of the Tanigan extra or Gerbstoff types. Rotanin BNS, produced in largest quantity, corresponds to Gerbstoff Que. Of the total tannin used, syntans constitute from 25% for sole to 11% for heavy shoe upper leather. The proportion of syntan used for sole leather is expected to reach 39% in 1960. Harness leather has been made successfully in pilot tests with 70% syntan. Formulas, procedures, analyses, and physical test data are given.

EXCHANGE SYNTANS IN CZECHOSLOVAKIA. Ivan Binko (*Leather and Allied Trades Research Inst., Gottwaldov,*

Čzech.). *Věda a výzcuu v průmyslu kožedělném* 3, 5-23 (1958); *Chem. Abst.* 52, 19202 (1958). Production of exchange syntans (I) was introduced because of difficulties in importation of vegetable tannins and declining production of spruce bark. Ratio of I to total tannin consumed had to be reduced in 1955 from 32 to 25% because of declining quality of sole leather. In 1956 there was used 10% of K₂D/K and SP/K, 3% K₁D/K, and 10% Kortan Q on pelt weight. Raw materials for I include raw, turbid phenols from soft-coal tars (indicated by K attached to symbol for I), 2-naphthol from naphthalene, and very large quantities of dihydroxybenzenes (Difen or Optol), mostly pyrocatechol and its homologs. Ligninsulfonic acid is regarded as a very poor base for I, and use of I containing ligninsulfonate is declining. The tendency is towards production of only the best I, based on dihydroxybenzenes, eliminating the older brands. Figures are given for raw materials used in various syntans. The SO₃H content should be kept to a minimum; this limit has perhaps been reached in SN₂₅ made from PhOH 32.7, HCHO 26.8, H₂SO₄ (92.5%) 10.1, and NaOH 3.8%. The decrease in acidity during tannage of tan liquors containing I can be minimized by neutralization with NH₃ and subsequent acidification with AcOH, as in Kortan Q₁ and QD, but then the hides swell unduly towards the end of tannage. The next goal is to produce I without any—SO₃H groups. Another aim is to produce I that is cheaper than vegetable tannin. Only the necessity of disposing of the raw, turbid phenols from coal tar, together with the crude dihydroxybenzenes, makes it possible to produce K₂D/K and SP/K at a price lower than vegetable tannin.

OBTAINING BETTER INDIGENOUS TANNING MATERIALS AND REDUCING THEIR IMPORTATION BY USE OF SYNTANS. George Havas and Nicolas Sucitulescu (*Leather and Rubber Research Inst., Bucharest, Romania*). *Kožářství* 7, 163-5 (1957); *Chem. Abst.* 52, 19207 (1958). Principal Rumanian tanning materials are spruce bark, oak bark, and oak wood. If importation of tannin should be forbidden, spruce would constitute 70% of available tannin, and a too lengthy tannage would be necessary. Preliminary work has been done on condensing PhOH or cresol and spruce tannin by HCHO, but production of syntans has been found the best solution. The development work is described. Romatan BCF is a condensate of PhOH and 2-naphtholsulfonic acid; BD is a dihydroxydiphenylsulfone condensate, dissolved in 2-naphtholsulfonic acid; CL is a condensate of ligninsulfonic acid

with cresolsulfonic acid and PhOH; RL is a PhOH-HCHO resin dispersed in a partly desulfonated and demethylated ligninsulfonic acid. Tanning with the Romantans is described and their analyses are given.

ROMATAN SYNTANS FOR TANNING SOLE LEATHER IN ROMANIA. *Nicholas Sucitulescu and Ion Dimitrescu (Ministry Light Ind., Bucharest, Romania). Kůžařství 7, 49, 74-5 (1957); Chem. Abst. 52, 19207 (1958).* Pilot-plant tests with Romatans are described. Romatan (10-40%) was added to tan liquors made up initially from 5 vegetable tannins and a little U.S.S.R. exchange syntan. The permissible maximum of Romatan is 30%, perhaps 40% for Cr-vegetable leathers. The use of Romatan was restricted to the suspenders and layers; the drum liquors contained only vegetable tannin, and therefore a less hydrophilic leather was obtained.

ZIRCONIUM TANNAGE—A review of the literature relating to Zirconium tannage. *D. A. Williams-Wynn, J.S.L.T.C. 43, 76-82, (1959).* The literature relating to zirconium tannage has been reviewed. Factors affecting the fixation of zirconium salts like pH, basicity, influence of concentrations, effect of salts on the uptake of zirconium by pelt and also the effect of the modification of the collagen have been discussed in the light of the recent work done in England, United States and France. The conclusions reached regarding the mechanism of the tannage was that neither deamination nor inactivation of the carboxyl groups affected the uptake of zirconium. This is quite different from the effect on chrome fixation where co-ordination with carboxyl groups is the principal reaction. Particular attention has been paid to published work dealing with the practical aspects of this tannage, including pickling, basifying, neutralising, dyeing and fat-liquoring.

T. S. R.

THE PRODUCTION OF CHROME-VEGETABLE TANNED LEATHERS. *Ludvik Kucka and Miroslav Minarik (SVIT, Otrovice, Czech.) Věda a výzcum v průmyslu kůžedělném 3, 79-88 (1958); Chem. Abst. 52, 19204 (1958).* Four types are distinguished: (1) Pretannage with 0.5-1.0% Cr_2O_3 and retannage with vegetable tannin (I) or (I) plus syntans (II), for sole, mechanical and heavy upper leathers; (2) pretannage with 1.2-1.8% Cr_2O_3 and retannage with II, or II + I, for fancy and lining leathers; (3) pretannage with I, or with II + I, and tannage with Cr salts, for

special leathers, e.g., shrunken grain; (4) pretannage with II, tannage with Cr salts, and retannage with I + II for pasted side upper leather. The Cr-vegetable procedure for sole leather, although used exclusively in U.S.S.R., is the most questionable. Details of this process are given; it includes a conventional liming, partial deliming, pickling, light Cr tanning, and vegetable tanning in 1 or 2 drums for 3 days, by using 29% tannin (80% oak-wood extract and 20% II) in strong liquors at 22-40°. Loss of I and II is 6.5%. A modified process, involving tannage in 3 suspender liquors and 2 drums, reduced the loss to 3.5-4.5% compared to 2.3-2.8% for purely vegetable tannage. The properties of Cr-vegetable sole leather are not greatly different from purely vegetable-tanned sole. Tensile strength is 10% lower but complies with standards; resistance to wet abrasion is higher but to dry abrasion is lower. Cr-vegetable tanned upper and liming leathers are decidedly superior to straight vegetable leathers.

PROCESSES AFTER TANNING

INVESTIGATION AND SELECTION OF BEST METHODS OF TECHNOLOGY OF PREPARATION OF SEMIFINISHED PRODUCTS FOR MANUFACTURE OF PATENT LEATHERS. P. M. Khokhlov. *Materially Obshchesty. Tech. Smotra po Proizd-stvu Lakovykh Kozh* (Moscow: Gosudarst. Nauch-Tech. Izdatel. Ministerstva Prom. Tovarov Shirok. Potrebleniya S.S.S.R.) *Sbornik* 1955, 10-31; *Referat-Zhur.*, *Khim.* 1956, Abstr. No. 34616, *Chem. Abst.* 52, 19205 (1958). A critical survey of processes of manufacturing patent leathers from goat skin is made from the standpoint of the effect of methods on the uniformity of finished leather. It is recommended that toggling be omitted and that drying should be done by the pasting process. After completion of drying, treatment by sawdust should follow. Proper neutralization is stressed. Good results are obtained when egg yolk is used for fat liquoring and also vegetable retanning after fat liquoring. Remarks on other methods are given.

FUR DYEING BY OXIDATION DYES. Frigyes Brugger and Lad, Paris (*Leather & Allied Trades Research Inst., Budapest, Hung.*), *Kožarství* 7, 354-7 (1957); *Chem. Abst.* 52, 19208 (1958). Conditions for the oxidation of *p*-phenylenediamine (I) by H_2O_2 in the presence of $K_2Cr_2O_7$ (II) were studied by determining the weight of insoluble oxidation products (III) formed. Maximum catalytic effect was attained with 0.05 oxidative equivalent II per I. A 3% solution of II was added to a solution of I in a thermo-

stat. Half the H_2O_2 (3% solution) was added after 1 hour; the other half after 2 hours. The temperature was maintained for 2 hrs. longer, after which the mixture was cooled overnight and III determined. In the presence of II maximum III was formed with 3 equivalents H_2O_2 (less III with more H_2O_2), and the temperature was without effect from 30 to 60°. In the absence of II, III increased with temperature, and the maximum III attained with 6 equivalents H_2O_2 was only 25-50% of the maximum attained with II. Chromic salts have the same effect as II, which is a significant point in dyeing lambskins tanned with chromic salts. In the absence of II, addition of NH_4OH gives a deeper shade, but the reverse is true in the presence of II. Dispersion of III is greater in the presence of NH_4OH . When PhOH is added to I, the weight of III is increased, but not in proportion to the weight of PhOH added. The oxidation products of I plus PhOH contain less N, are less soluble, and therefore better suited to dyeing than III. Pyrocatechol and resorcinol apparently act the same as PhOH but possess no advantages.

THEORIES

THE MODE OF CO-ORDINATION OF AMINO ACIDS WITH CATIONIC CHROMIUM IN ACID AQUEOUS SOLUTIONS—SPECTROPHOTOMETRIC STUDIES I—S. G. Shuttleworth and R. L. Sykes, *J.A.L.C.A.* 54, 259-68 (1959). Spectrophotometric curves on chromium complexes formed with α -, β -, γ - and ϵ -amino acids at 1, 2 and 3 moles/mole chromium and aged to equilibrium at pH 2.50, 3.16, and 3.82 show that the molar extinction coefficients increase from the α to the ϵ forms, which is opposite to the effect which could be anticipated from chelation of both carboxyl and amino groups. The extent of co-ordination, as revealed by the spectrophotometric curves, appears to be approximately proportional to the pK values of the carboxyl groups, which are influenced by the number of carbon atoms separating the carboxyl and amino groups. A similar pattern is revealed by studying the fixation of chromium by pelt from solutions masked with α -, β - and γ -amino-n-butyric acids, the masking power increasing from α to γ . These results also appear to confirm the suggestion of one of the authors that the stability of co-ordination of an acidic group to chromium is inversely related to the dissociation constant of the acid.

SOME NOTES ON THE PROBLEM OF THE PREPARATION OF PURE FIBROUS COLLAGEN. C. Deasy, *J.A.L.C.A.* 54,

246-58 (1959). In much work that is of interest to the leather chemist the properties of fibrous collagen, the protein that is the chief component of the skin, are of importance. Therefore, it is useful, and in some work essential, to use a fibrous collagen preparation which is as pure as possible in order to study these properties. Since fibrous collagen is a protein which is insoluble in most solvents and dissolves only in those solvents in which it is probable that some degradation occurs, its purification is much more difficult than that of most proteins, which can be purified by repeated solution and precipitation.

The present paper will assess the problem of purification from two points of view: (a) that components of the skin other than fibrous collagen which must be removed in the purification, and (b) the methods of purification which have been used up to the present time. It should always be borne in mind that a method of purification is not necessarily successful if it has removed all the other foreign matter; it should also leave the fibrous collagen in the undegraded or native state.

TESTING

CONCENTRATION DEPENDENCE OF SEDIMENTATION FOR GELATIN. D. L. Woernley, F. C. Wissler, C. Carruthers, and K. T. Lilga (Roswell Park Mem. Inst., Buffalo, N. Y.). *Phys. in Med. Biol.* 2, 346-53 (1958); *Chem. Abst.* 52, 19208 (1958). The concentration dependence of sedimentation of purified calfskin is accurately determined in order to ascertain the existence of a reciprocal relation between sedimentation rate s and relative viscosity. The graphs of s and l/s vs. concentration at 30° are not linear throughout the range of 0-1.5% gelatin, the deviation increasing with growing concentration. The reciprocity assumption is not obeyed, with marked aberrations in the range 1.0-1.5%. The sedimentation constant is 3.9 (S units), the intrinsic viscosity amounts to 0.61.

NEW COMPLEXONE EGTA SOLVES AN OLD PROBLEM. T. S. West, *Chemical Age*, 81, 405 (1959). A new complexometric procedure making use of ethylene glycol-bis (β -amino ethyl ether) N,N,N',N' tetra acetic acid has considerably simplified the determination of calcium in presence of large amount of magnesium. A successful indicator has been found in Zircon, sensitised with Zn-EGTA complex for carrying out the titration.

A method has been developed for the coulometric determination of water with electrically generated Karl Fischer Reagent. The method has several attractive features such as determination of water at concentrations less than 1 mg/ml.

D. R.

THE DETERMINATION AND FRACTIONATION OF SULFATES IN WATER SOLUTIONS OF CHROME ALUM. Anton Blazej and Aloib Mracna (*Tech. Univ. Slovakia, Bratislava, Czech.*). *Kožařství* 7, 324-8 (1957); *Chem. Abst.* 52, 18088 (1958). The determination of total, cold- and warm-titrated, and also free SO_4^{--} ions was studied. Total SO_4^{--} was determined, gravimetrically with benzidine dichloride. Cold- and warm-titrations were made with phenolphthalein. The cold titration determines free $\text{H}_2\text{SO}_4^{--}$ bound electrovalently to cationic Cr complexes, and a part of co-ordinatively bound sulfate. During the potentiometric titration with Sb or glass electrodes 4 points of inflection appear at pH 3.3 and 8.5; the 1st gives free H_2SO_4 . Solutions with pH under 2.8 always, solutions with pH 2.8-3.3 sometimes, and over pH 3.3 never contain free H_2SO_4 . The titration of a boiling solution gives free and complex bound SO_4 (a determination of basicity). Total SO_4 is determined gravimetrically by the Hintz and Weber method.

DETERMINATION OF ORGANIC ACIDS BY PAPER PARTITION CHROMATOGRAPHY. Kh. U. Usmanov, A. M. Yakubov, and R. S. Tillaev. *Doklady Akad. Nauk Uzbek. S.S.R.* 1956, No. 5, 23-5; *Referat. Zhur., Khim.* 1957, Abstr. No. 8584. *Chem. Abst.* 52, 18094 (1958). The absorption of organic acids during partition chromatography on paper causes the formation of "comets" (the acids do not move in narrow bands but trail each other) which complicates the identification of the acids. The addition of small amounts of a volatile acid (e.g., HCOOH or AcOH) to the mobile phase markedly decreases the absorption and reduces the effect of concentration on the moving of bands. The possibility of chromatographic identification and quantitative estimation of organic acids was established by the determination of 46 aliphatic and aromatic acids (by using a water-saturated solution of BuOH containing 5% HCOOH as the solvent, and a 0.04% alc. solution of bromocresol blue as the developing agent). Rosolic, picric, and aminopicric acids do not require a developer for their qualitativ. determination since they form characteristic coloured spots.

FATTY-ACID AMIDES. III. PAPER CHROMATOGRAPHY OF FATTY-ACID AMIDES. H. P. Kaufmann and K. J. Skiba (*Inst. Fettforschung, Munster, Ger.*). *Fette. Seifen, Anstrichmittel* **60**, 261-3 (1958); *Chem. Abst.* **52**, 19183 (1958). The separation of fatty-acid amides, C_{10} - C_{18} , is carried out by paper chromatography as described for the corresponding acids with 70% HOAc and $C_{11}H_{24}$ as developer at 20°, identifying the products by immersing the completed chromatograms in a 3% solution of $Hg(OAc)_2$ acidified with HOAc, washing with H_2O , drying, and spraying with 0.1% diphenyl carbazone in EtOH, giving a bluish background which fades with several hours, leaving blue amide spots visible for several weeks. R_f values for the following acid amides are given capric 0.80, lauric 0.66, myristic (I) 0.53, palmitic (II) 0.29, stearic: 0.15, oleic (III) 0.31, elaidic 0.24, linoleic (IV) 0.44, linolenic 0.62. Mixtures of II and III and of I and IV could not be separated.

POTENTIOMETRIC TITRATION OF WEAK ACIDS IN NONAQUEOUS SOLVENTS. D. H. Mathews & T. R. Welch. *J. Appl. Chem.* **8**, 701, 711 (1958). A potentiometric technique in nonaqueous medium has been described which is suitable for the estimation of carboxylic acids in a 'neutral solvent' such as a mixture of benzene and methanol, and for the estimation of weaker acids such as phenols in basic solvents such as *n*-butylamine or a mixture of benzene and ethylenediamine.

The reproducibility of the procedure has been shown to be about $\pm 1.25\%$ of the volume for a neutral solvent and rather more for a basic solvent owing to carbon dioxide interference. Suitable electrode assemblies were worked out for hydroxyl substituted benzoic acids and dihydric phenols. The results and their limitations are discussed taking into account electron-attracting and electron-repelling properties of substituent groups and the resultant effects on acid strength.

D. R.

SIMPLE METHOD FOR THE DETERMINATION OF WATER-SOLUBLES CONTENT OF LEATHER. Satoshi Sawayama, Kazuhiko Ito, and Minoru Satani. *Hyogo Noka Daigaku Kenkyu Hokoku* **3**, 9-11 (1957); *Chem. Abst.* **52**, 19205 (1958). Ground leather (15 g.) was digested with 300 ml. H_2O in a 500-ml. Erlenmeyer flask at 35, 40, 45, or 50° for 2 hrs. by shaking once in every 30 minutes. The filtered residue was further digested with

100 ml. H_2O for 1 hr. The combined extract was made to 500 ml. at room temperature, filtered, and 50 ml. of the filtrate was evaporated and dried to constant weight at 100-5° to obtain H_2O -soluble content (I). From the curve of extraction temperature vs. I, the values of I at 38° and 49° agreed well with those obtained by the ALCA and the SLTC methods.

TANNIN-DECOMPOSING ENZYME OF MOLDS. VII. APPLICATION OF COLLOID TITRATION METHOD TO THE MEASUREMENT OF THE ACTIVITY OF TANNIN-DECOMPOSING ENZYME. Hiroshi Nishira, Ryu Shinke, and Narataro Mugibayashi. *Hyogo Noka Daigaku Kenkyu Hokoku* **3**, 43-6 (1957) (in English); *Chem. Abst.* **52**, 18614 (1958). The activity of tannin-decomposing enzyme was determined by the colloid titration method of Nakabayashi. The reaction mixture (containing 1.5-2.0 mg. tannin) was dialyzed through cellophane for 24-50 hrs. and then the residual tannin was determined by colloid titration. The enzyme activity could be established from the relation between reaction time and residual tannin. An enzyme solution from *Aspergillus niger* showed a minimum tannin at 4 hrs. of reaction and a maximum tannin at 5 hrs. Tannin-related substances were considered to be synthesized by the enzyme solution at that stage.

SPECTROPHOTOMETRIC DETERMINATION OF ELASTIN. V. Scarselli (*Univ. Milan*). *Giorn. biochim.* **7**, 20-7 (1958); *Chem. Abst.* **52**, 18619 (1958). Take 0.5 g. tissue or organ, mince it to 1 mm. particles, wash with H_2O to free from blood, filter, add this homogenate to acetone (1.5 g. per 100 cc.), leave at room temperature, decant, change solvent, leave for 7 hrs., decant, extract with 50 ml. Et_2O for 12 hrs., dry at 70° for 14 hrs., triturate the dry matter, take 40-50 mg., macerate in 10 ml. 0.1N NaOH at 25° for 8 hrs., centrifuge for 20 minutes, decant, wash with 10 ml. EtOH at 38° for 20 minutes, centrifuge for 10 minutes, decant, add 10 ml. alc. solution orcein (1 g. orcein in 100 ml. abs. EtOH; add 1 ml. HCl (d.1.19); dil. 1 to 10 with EtOH for the use) per 2.5 mg. supposed elastin, leave at 25° for 24 hours. (occasional stirring), centrifuge for 20 minutes, decant, wash several times with 10 ml. EtOH at 25° to complete (labile) color removal, evaporate alc. traces off at 38°, and 5 ml. carbonate buffer (pH 10; mix equal volumes of 0.05 M solutions of carbonate), leave at 38° for 3 hrs., digest with 5 ml. pancreatin 4% solution at 38° for 45 minutes (occasional stirring), centrifuge for 15 minutes, leave for 1 hour at room temperature, read optical d. by a spectrophotometer at 590 m μ in comparison with a blank prepared with 5 ml. buffer

and 5 ml. pancreatin solution, and calculated by a standard curve. With elastin concentrations of 5 mg./100 g. of dry organ, the method has a standard deviation of 1%. The sensitivity of the method is 0.067 mg. elastin. By the above method the following elastin contents were determined (in per cent of dry tissue or organ): ox tendon 0.28, rat brain 0.30, rat liver 0.44, rat muscle 1.35, rat heart 2.52, rat spleen 3.22, ox lung 3.46, rat lung 5.19, cat lung 5.25, and human aorta 45.32.

THE STRATIGRAPHIC DISTRIBUTION OF DRY MATTER AND NITROGEN IN CATTLE HIDES. *Edward F. Mellon, Samuel J. Viola, Alfred H. Korn and J. Naghski. J.A.L.C.A. 54, 182 (1959).* A precision slicing technique was employed to cut consecutive slices of equal thickness parallel to the grain surface of a cattlehide. These slices were analyzed to determine the quantitative distribution of various components through the thickness of the hide. A dehydration procedure was developed which enabled the contents of these slices to be calculated on dry-weight basis. The dry-weight yield and the nitrogen content of the slices revealed marked differences in composition through the thickness of the hide. The flesh and grain areas contained less dry matter than the corium. A similar trend was also evident from the nitrogen values.

A STUDY OF COLD CRACKING TESTS FOR UPHOLSTERY LEATHERS, *Robert J. Fopma, J.A.L.C.A. 54, 194 (1959).* A series of tests was conducted to evaluate four methods of cold testing for upholstery leather. These were the Impact Test, Hand Fold Test, Newark Cold Flex Test, and the Greuel Rotary Cold Fold Test. The main purpose of the experiment was to determine differences among the tests and to find which test was most satisfactory as to reproducibility, variation in results among laboratories or due to other factors, and speed and economy in testing. It was determined that the Greuel Test, on the average, produced cracking at a lower temperature than the other three but showed much less variability. As this test is faster, cheaper, and much easier to perform, it was adopted as the official test of the Upholstery Leather Group for determining cracking at low temperatures, and industry specifications were adopted for its use.

BYE-PRODUCTS

UNEXPLOITED RAW MATERIALS FOR GELATIN PRODUCTION. *Jarmila Zlamalova (Vyzkumny ustav pro maso a*

ryby, Brno, Czech.). Chem. primysl 8, 132-6 (1958); Chem. Abst. 52, 19208 (1958). In exploratory experiments, conventionally used technological processes yielded gelatin from hitherto unexploited raw materials. Yields and organoleptic properties of the various gelatins are reported. Pig legs and hides, calf legs, and bovine sinews (from bones) yielded nutritional-grade material. Bovine penes were found to be a suitable source for technical-grade gelatin. Calf heads, vaginae, and eye-balls were found to be unsuitable for gelatin production.

PATENTS

TANNINS FROM SULFITE WASTE LIQUORS. *Fritz Stather and Guntur Reich., Ger. (East) 9949, Dec. 8 1955 (Cl. 28a, 6), Chem. Abst. 52, 19210 (1958).* Tannins capable of tanning without any addition are prepared from sulfite waste liquors under normal pressure by heating with so little alkali that, during the whole reaction period, the reactants remain fluid. The tannin is separated from the solution by means of an acidified salt solution. For example, 1000 g. purified sulfite waste liquor (32° Bé.) was mixed with 100 g. NaOH and heated to 100° for 5 hrs. with stirring. The hot solution was introduced into a saturated (NH₄)₂SO₄ solution and acidified to pH 3.5 with 50% H₂SO₄. The granular ppt. was filtered off and dissolved in twice the amount of water. Upon addition of 3% AcOH, the preparation of tannin was complete.

SYNTHETIC INTERCHANGEABLE TANNING AGENTS. *Fritz Stather and Guntur Reich. Ger. (East) 9989, June 30, 1955 (Cl. 28a, 6), Chem. Abst. 52, 19210 (1958).* From untreated or alkali-treated sulfite waste liquors, tanning agents capable of tanning without any addition are obtained by condensation with HCHO and multi-valent technical phenols at elevated temperatures. For example, 1 M pyrocatechol was mixed with 100 g. pure tannin from acid-purified sulfite waste liquor (32° Bé.) and brought to pH 2.4. Within 1 hour, 0.5 M HCHO (30%) was added at 80° with agitation and condensed at 100° for 6 hours. **Ger. (East) 10,016, July 4, 1955.** Lignophenols from the alkali melting or pressure boiling of sulfite waste liquor are treated in an alkali medium with a sulfite, HCHO, and mononuclear multi-valent phenols. The tanning agents thus obtained are soluble in cold water. Thus 1000 g. alkali-cleaned sulfite waste liquor (32° Bé.) and 1000 g. NaOH were heated to 180° for 2 hours. The melt was dissolved in water, acidified to pH 3.5 with HCl

and the lignophenol (I) filtered off and dried. I 100 and pyrocatechol 25 were dissolved in 125 g. aq. 10% NaOH, 25 g. Na₂SO₃ added, and heated to 90°. Then, 125 g. 30% HCHO was added and the mixture condensed at 100° for 4 hours. After introduction into saturated (NH₄)₂SO₄ and bringing to pH 3.5 with H₂SO₄, the reaction product was precipitated.

TREATMENT OF LEATHER. *Cassella Farbwerke Mainkur Akt-Ges. Wilhelm Kunze, Arthur Miekeley, and Georg Kolling, (Inventors).* Ger. 949, 591, Sept., 20, 1956 (Cl. 28a, 9); Chem. Abst. 52, 19210 (1958). The quality of leather is improved by treating the leather with an aq. polymer emulsion obtained by the reaction of 70-85 parts (by weight) asym. dichloroethylene with 30-15 parts Bu acrylate with the addition of Na paraffin sulfonate in the presence of a reduction-oxidation system of Na formaldehydesulfoxylate and H₂O₂.

SYNTHETIC LEATHER. *Bertha Jaehner.* Ger. 922,410, Jan. 17, 1955 (Cl. 81,2); Chem. Abst. 52, 19260 (1958). Porous synthetic leather is made by pressing together fibrous sheets with foils of thermoplasts. The foils are perforated so as to allow circulation of moisture and air. The foils and the fibrous material may be rendered moistureproof and resistant to bacteria by suitable impregnation before pressing.

LEATHER SUBSTITUTE. *Tsentrāl'nyi Nauchno-Issledovatel'skii Institut Promyshlennosti Zamenitelei Kozhi. U.S.S.R.* 111,168, May 27, 1958; Chem. Abst. 52, 19260 (1958). A leather substitute is made from a carboxylate rubber containing varying amounts of polar groups. This is combined with substances, such as poly (vinyl chloride), nitrocellulose, polyamides, poly (vinyl acetate), or proteinaceous matter.

HIGH POLYMERS WITH QUARTERNARY AMMONIUM GROUPS. *Badische Anilin & Soda-Fabrik Akt.-Ges. (Curt Schuster and Robert Gehm., inventors).* Ger. 941,999 Apr. 26, 1956. Chem. Abst. 52, 19256 (1958). N-vinylimidazoles, such as N-vinylimidazole and its substitution products, N-vinylbenzimidazole, and N-vinylnaphthylimidazole, are polymerized either with themselves or with other polymerizable compounds (I) and form polymeric tertiary bases, which are condensed to quaternary ammonium compounds (II). Suitable I are styrene, vinyl chloride, as-ethylene dichloride, vinyl acetate, acrylonitrile, and esters of acrylic, maleic, and fumaric acid. The polymerization occurs

in a usual manner with peroxide catalysts and heating in a solvent, such as water or organic compounds. In many cases II is obtained in a solid state. II is soluble in water and capable of being used in the textile industry. For example, 86, parts diethyl maleate (III) and 47 parts N-vinylimidazole (IV) were dissolved in 200 parts dioxane, and then 6 parts 30% aq. H₂O₂ is added. At 70-80° polymerization occurred in the next 15 hrs. Then 63 parts Me₂SO₄ was added to the solution. The tough precipitated product (V) was separated from dioxane. V was the polyquaternary salt of a copolymer from III and IV. V was water-soluble.

POLY (ESTER AMIDES). *Dr. Beck & Co. G.m.b.H.* Brit. 796,008, June 4, 1958; Chem. Abst. 52, 19254 (1959). Polyesteramides, containing free hydroxyl groups, are manufactured by treating di-Me terephthalate (I) with at least 1 linear diamine, e.g., H₂N (CH₂)₄NH₂ or H₂N(CH₂)₆NH₂ (II), and at least 1 polyol, e.g., glycerol, tris (hydroxymethyl) propane, or pentaerythritol. Thus, I 194, glycerol 92, and II 58 parts by wt. are melted in an atmosphere containing CO₂ to form a homogeneous substance which is refluxed under stirring for 1 hr. The temperature is raised to 240° to distill off the MeOH, and condensation is continued to yield a clear, elastic, and nonadhesive resin. By adding cresol to the reaction product, a 40% solution is obtained for varnishing Cu wire. Addition of adipic or sebacic acid and of ethylene glycol, 1, 3-propanediol, or 1, 4-butanediol to the mixture is also described and (or) claimed.

POLYAMIDES. *Farbwerke Hoechst A.-G. vorm. Meister Lucius & Bruning (Paul Schlack, inventor).* Ger. 930,286, July 14, 1955; Chem. Abst. 52, 19254 (1958). Various types of linear or cross-linked high-molecule polyamides are prepared by condensing di- or polyamines with di- or polycarboxylic acids, or polyfunctional amino carboxylic acids with themselves, provided that at least some of the acid groups are esterified with mercaptans. Approximate equivalent amounts of NH₂ and COSR groups (in the same or different molecules), give linear superpolyamides (fibers). Solvents, diluents, or fluxes may be used. Bases accelerate the polymerizations, especially toward end of the reaction when few of the basic NH₂ groups from the starting material are left. Esters of volatile mercaptans are normally used, but hexyl, dodecyl, phenyl, or benzyl thio esters can be used when the degree of polymerization desired is not high or when the reaction can be

run at high temperatures and low pressures. Normal alkyl esters are not reactive enough. Aromatic esters yield phenols as by-products which are hard to remove from the polyimide melt. Thiophenols have a much lower affinity for polyamides than phenols. For linear polymers, the higher reactivity of their thio esters allows α - and β - amino acids to be used: however, usually >5 C atoms between the NH_2 and the COOH groups are desirable, e.g., 9-aminononanoic or 11-aminoundecanoic. The amino acid thio esters are set free gradually from their acid salts in the reaction mixture by evaporation of the acid (CO_2 or H_2S) or by addition of tertiary amines or Na caprolactamate. Thio esters of dicarboxylic acids give a low degree of polymerization and are generally used with N_2H_4 derivatives or secondary diamines (which cannot form amide linkages directly) but allow use of low reaction temperatures. Partially polymerized polyesters with thio ester end groups can also be used as starting material; the COSR groups react with di- or polyamines giving products of higher m.p. insolubility and crystallinity. Part of the thio esters can be replaced by other reactive poly-functional acylating agents. Other permissible additives include polymerizable lactams or amino acid esters. The amines used must have 2 or more basic NHR groups. Solvents are generally used with bifunctional monomer mixtures and foster the production of high-molecule linear polymers without cross-linking. Reactants, e.g., casein, giving insoluble cross-linked products are applied, separately if desired, to bases, such as sawdust, fibrous materials fabrics, or paper, homogenized or polymerized, and then heatpressed in the presence of plasticizers or softeners. The reaction temperature lies between 20 and 250° , generally 100 - 200° . Esters of methylthiol and diamines $[\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2]$, where $n=2$ or more] have optimum reactivity. The high reactivity and low m.p. of such mixtures make them especially suitable for continuous processes in which the monomer mixture is allowed to flow in a thin layer over a heated surface to ensure speedy removal of mercaptans liberated during reaction. If the amines are volatile, either an excess is added at the start to allow for their partial evaporation with the thiols, or the first stage of the polymerization is run under pressure. The mercaptans are recovered either by condensation or by absorption on kieselguhr. In general, the polymers can be used for the production of fibres, films, or coatings, or for thermoplastic moldings (cross-linked polyamides). When esters of mercaptans containing hydrophilic groups, e.g. esters from dicarboxy-

lic acids and thioglycolic acid or 2-mercaptoethyldiethylamine, are used, cross-linked polyamides are obtained which can be molded or produced directly on substrates, e.g. for animalization purposes. In an example, terephthaloyl chloride (I) plus NaSEt gave $\text{p-C}_6\text{H}_4(\text{COS Et})_2$ (II), white platelets, m. 89 - 9° , from AcOH: II (51.7 parts) added with stirring to 41.75 parts tetramethylenebis (3-aminopropyl) ether reacted immediately with vigorous evolution of EtSH. The mixture was then heated under N for 80 minutes to 220° and kept at this temperature for 0.5 hrs. and then at 230° for 0.5 hrs. The pressure was then reduced to 100 mm. for 20 minutes. The yellow, tough polymer melt obtained could be stretched to strong threads of softening point 190° , m. 200 - 10° . When di-Et terephthalate was used instead of II, much longer heating times were required.

COBALT COMPLEXES OF MONOAZO DYES. Robert F. M. Sureau and Georges R. H. Mingasson (to Compagnie française des matières colorantes). U.S. 2,840,552, June 24, 1958; Chem. Abst. 52, 19149 (1958). Dyes of the formula $\text{RN:NCH}(\text{CONHR})$; COMe, in which R is the residue of a diazotizable base containing in ortho position a group capable of being metalized, but no SO_3H or COOH group elsewhere, and R' is a heterocyclic nucleus, especially a benzothiazole group, are obtained by diazotizing suitable amines and coupling them with $\text{R'NHCOCH}_2\text{COMe}$. The products are then metalized. Groups ortho to the diazotizable NH_2 function include OH, OMe, OCH_2COOH , and COOH , and the coupler can contain haloalkyl, OMe, NO_2 , R''CONH , ArCONH , $\text{SO}_2\text{-NH}_2$, SO_2NHR , SO_2NHAr , RCO , and SO_2 groups. The dyes are useful in colouring organic solvents, lacquers, varnishes, and cellulosic esters and ethers, wool, silk, leather, animalized fibres, superpolyamides and superpolyurethans. Thus, 2-acetoacetamidobenzothiazole (I) 2.3 in water 30 and 36° Be. soda lye 2 is run into diazotized 2-amino-4-sulfonamidophenol 2.3 in water 50 parts at 0 - 5° , agitated at 30 - 40° for an hour, the solid (I) filtered, washed with cold water, and dried at 60° . I in water 50 at pH 10 is refluxed, and Na cobaltotartrate 7.5 parts is added. The dye is precipitated with NaCl, filtered, and dried. It dyes wool yellow from an NH_4OAc bath; the shade is fast to light and humidity. An orange-yellow shade is obtained if 5-chloro-6-acetamido-2-methylthiobenzothiazole is used instead of I.

FINISHING OF FIBROUS MATERIALS. Badische Anilin- & Soda-Fabrik Akt.-Ges. (Friedrich Holscher, Karl Craemer, and

Rudolf Schubert, inventors). Ger. 936,925, Dec. 22, 1955; Chem. Abst. 52, 19155 (1959). Fibrous material is treated with aqueous dispersions of polymers of unsaturated amides (I) and vinyl compounds containing active halogen atoms (II); the unsaturated amides are copolymerized with a vinyl compound which gives soft and ductile polymers if it is polymerized alone. The products are used for coating, impregnating, or printing of textiles or for leather finishing. Copolymers of I, II, and vinyl compounds which have plasticizing action are of particular value. For the preparation of I, amides of acrylic, methacrylic, and crotonic acid are used; and for II, *asym*-dichloroethane or vinyl chloride. The plasticizing vinyl polymers are made from Bu acrylate or vinyl isobutyl ether. The 15-60% (preferably 40-50%) dispersions of copolymers containing 0.2-15.0% (preferably 0.5-3%) I and the equivalent amount of halogen compounds are thickened with oil-in-water emulsions of non-watermiscible organic solvents (b. 75-220°) or conventional thickeners. Other adjuvants and dyes can be added. For leather finishing, 4-15% dispersions are used. Thus, 100 parts of a 40% aq. dispersion of a copolymer containing% 50 2-chloroethyl acrylate, 40% Me acrylate, and 10% acrylamide were mixed with 250 parts water containing 2 parts of the Cr complex of an azo dye prepared, from 2-amino-phenol-4-sulfonic acid and *m*-phenylenediamine. The solution gave a water- and rub-resistant high gloss finish to leather. Comparisons for textile impregnation and for printing ink are also given.

NOTES & NEWS

SEVENTH MEETING OF THE LEATHER SECTIONAL COMMITTEE OF ISI AT THE CENTRAL LEATHER RESEARCH INSTITUTE

The Seventh Meeting of the Leather Sectional Committee, CDC 16 of the Indian Standards Institution, in joint session with its five subcommittees was held on 28 and 29 May 1959 at the committee room of the Central Leather Research Institute, Adyar, Madras-20 under the chairmanship of Dr. Nayudamma, Director, Central Leather Research Institute and Chairman CDC 16. Prior to this the following subcommittees held independent sessions:

- (i) Glossary of Terms Subcommittee, CDC 16 : 6, 26 and 27 May 1959.
- (ii) Heavy Leather Subcommittee, CDC 15:2 27th May 1959.

Welcoming the members representing interests from all over the country, the Chairman complimented the Subcommittees for the excellent work accomplished by them in preparing the important draft Indian standards and in scrutinizing the numerous technical comments and observations received thereon from various quarters. Outlining the future pattern of work he stressed the imperative necessity for leather standards to take cognizance of varying local conditions and the ultimate object of improving quality primarily for the export market. Urging on members the extensive and difficult nature of the work involved in obtaining authentic analytical and scientific data from different parts of the country, the Chairman solicited the unstinted co-operation of regional testing and analytical laboratories, Small Scale Industries Organisations etc. Finally he hoped that realizing the All India character and the farreaching importance of the work of the Leather Sectional Committee of ISI, the State and Central Governments would not lag behind in making available the necessary finances to the regional laboratories to participate and contribute their share in this venture.

Dr. Sadgopal, Deputy Director (Chemicals) ISI and Secretary of the committee apprised the members of the major expan-

sion in the work of the chemicals division of ISI with special reference to the ever-increasing work in respect of the standardization undertaken by this committee in the field of hides, skins, leather and leather goods. This increased volume of work has of necessity reflected in very heavy demand and responsibility on the members.

The Secretary, further, thanked the Director, Central Leather Research Institute, who as Chairman CDC 16 was giving his best to the sectional committee's work; in fact his able colleagues were shouldering the work of CDC 16 and its subcommittees.

The Committee during its deliberations finalized the draft Indian Glossary of Terms Relating to Hides, Skins and Leather on the basis of the following general basic principles :

1. The glossary to be confined to terms strictly related to hides, skins and leather and deleting general chemical and other terms wherever necessary.
2. To defer inclusion of Hindi equivalents for the time being.
3. To delete all terms relating to proprietary and patented items from the draft glossary. In addition to these general directives given at the last meeting of CDC 16, the Subcommittee decided to adopt the following general principles :
 - (i) Wherever animal or plant names occur, the universally accepted scientific names to be given.
 - (ii) The presentation to be in dictionary style without words and without capitalisation of the first letter after the dash.
 - (iii) Inverted commas and quotations to be eliminated as far as possible.
 - (iv) Place names, e.g., *Agra*, *Kanpur*, when applied to classes of leather, to be underlined.
 - (v) Loose or ambiguous terms to be excluded.
 - (vi) The heading of the glossary being Draft Indian Glossary of Terms relating to Hides, Skins and Leather, terms relating to footwear and other trades to be excluded.
 - (vii) Suitable photographs and illustrations relating to important terms to be included.

The committee approved for wide circulation after elaborate discussion seven draft Indian Standards relating to :

- (1) Cycle saddle leather.
- (2) Waxed Chrome Sole leather.
- (3) Sizes and fittings of footwear.
- (4) Men's shoes, superior quality.
- (5) Men's shoes, popular quality.
- (6) Men's shoes utility quality and
- (7) Wax shoe polish.

The desirability of introducing the mildew test in the relevant Indian Standard method of test for leather was discussed. Inclusion of this test, along with revision of other methods of test if necessary, was entrusted by the Sectional Committee to its Methods of Test Subcommittee.

The Committee approved the following new subjects for formulation of standards for its future programme of work :

- (1) Leather for Flat, Round and V - Belting
- (2) Book - Binding Leather
- (3) Clothing and Lining Leather including Suede Leather
- (4) Postman Bags
- (5) Cash Bags for Railways
- (6) Holdall Straps
- (7) Gloves for Welders
- (8) Protective and Occupational Footwear
- (9) Mining boots
- (10) Special types of Leather required for Oil Seal, Washers, Diaphragms, brackets and other moulded articles
- (11) Leather for Sport Goods.

INDIAN STANDARDS CONVENTION 1959

Shri Lal Bhadur Shastri, Union Minister for Commerce & Industry is expected to inaugurate the fifth Indian Standards Convention, scheduled to meet at Hyderabad from 27 December 1959 to 2 January 1960. It may be recalled that the previous four Conventions were held at Calcutta, Bombay, Madras and New Delhi

respectively. A Reception Committee, under the Chairmanship of Shri C. S. Tyabjee, President of the Federation of Chambers of Commerce and Industry, Andhra Pradesh, has been formed to make arrangements for the delegates' stay and for various technical visits, and social and cultural programme.

Over 500 delegates are expected to participate in the deliberations of its nine technical sessions, covering subjects like the Implementation of Indian Standards; Standardization and Productivity; Design for Industrial Experimentation; Tropicalization of Electrical and Electronic Equipment; Latest Techniques in Chemical Analysis; Documentation; Certification for Small Industries Products, etc.

EAST INDIAN TANNED KIPS AND SKINS

A Draft Specification Ready for Comments

The Indian Standards Institution has issued a draft specification for East Indian Tanned Kips and Skins [Doc: CDC 16 (621)].

The draft lays down the requirements of East India tanned leathers for pure tannages, and includes all leathers under the category of prime tannages, semi-prime tannages, and single tannages.

The volume of export and the foreign exchange earning capacity of this industry is considerable, because the special attributes of East India tanned leather, such as its spread, colour, feel, homogeneity, well-set strippable nature and its great tensile strength, have earned for it a world-wide reputation.

Unfortunately, of late, some unscrupulous competitors, by adulterating the tanned hides and skins with extraneous materials, have posed a serious threat to the export potentialities of this leather.

In order to encourage the scientific development and a rational stabilisation of this Industry, this standard has been drafted, which is being circulated with a view to eliciting comments before 28 July, 1959. Experimental data, collected for a large number of samples and conducted at the Central Leather Research Institute and at the Laboratory of the Development Wing, Ministry of Commerce & Industry, have been used in drafting this standard.

Copies of the draft are available, free on request, from the office of the Indian Standards Institution, New Delhi, or from its Branch Offices at Calcutta, Bombay and Madras.

LEATHER PUMP BUCKETS

An Indian Standard Issued

The Indian Standards Institution has published, as a part of series of Indian Standards on leather and leather goods, a Specification for Leather Pump Buckets Made from Chrome Tanned Leather (IS: 1273-1958). This standard prescribes the requirements of leather pump buckets made from chrome tanned leather, for use in water system, when temperature is likely to be higher than the normal temperature.

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

SPECIFICATION FOR ONE-MARK PIPETTES

An Indian Standard Issued

The need for standardization of one-mark pipettes has been keenly felt by manufacturers as well as by scientific workers both in industries and in scientific laboratories. With a view to meet this demand, the Indian Standards Institution has published an Indian Standard Specification for One-mark Pipettes IS: 1117-1958.

This standard prescribes the requirements and the methods of test for one-mark pipettes, which are used for delivering fixed quantities of liquids.

This standard prescribes two series of tolerances on the capacity of pipettes, namely Class A and Class B. The Class A has been laid down to meet the requirement of pipettes of reasonably high accuracy, while Class B is designed to have an accuracy suitable for general purposes.

Copies of the standard, published in English and priced at Rs. 2.00 each, are available from the offices of the Indian Standards Institution, located at New Delhi, Bombay, Calcutta and Madras.

*Annual Day Celebration of the Government Leather Institute,
Kanpur*

Annual day of the Government Leather Institute, Kanpur was held on Sunday, May 10th, 1959. Dr. Kripa Shanker, Deputy Director of Industries (Technical Education Section), U.P., presided on the occasion and Col. Nilakantam, Chief Superintendent of Development (T & C), Ministry of Defence, Kanpur, distributed prizes.

Sri K. L. Muir, Principal of the Institute welcomed the gathering and reviewed the achievements of the Institute.

Col. Nilakantam appreciated the good sporting spirit demonstrated by the students and staff.

The President, in his remarks explained the interest of the Government in the development of Technical Education in the country and drew attention to the financial help given to the Institute by the State and Central Governments.

Sri G. Roy Choudhury, Vice-Principal of the Institute proposed a vote of thanks.

RESEARCH BEARS FRUIT

Practical Demonstration No. 7

(Third Series)

Process : Manufacture of Football leather.

Period : 27th July to 6th September, 1959.

Place : Central Leather Research Institute.

A process for the manufacture of Football leather 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 the 27th July to 6th September, 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.

Practical Demonstration No. 8

(Third Series)

Process : Manufacture of Chamois leather using Sardine Fish Oil.

Period : 3rd August to 29th August, 1959.

Place : Central Leather Research Institute.

A process for the manufacture of Chamois Leather using Sardine Fish Oil 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 the 3rd August, to 29th August, 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 your 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.

C. L. R. I. NEWS

Dr. Y. Nayudamma, Director, Central Leather Research Institute has been nominated principal member of the Working Group for Leather and Allied Industries under the Committee for Heavy Industries Plan set by the U.P. State.

Dr. S. K. Barat, Assistant Director, Central Leather Research Institute has been nominated as Alternate member of the Working Group for Leather and Allied Industries under the Committee for Heavy Industries Plan set by the U.P. State.

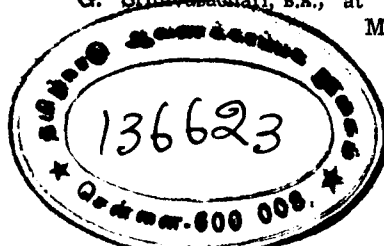
Dr. Y. Nayudamma, Director, attended the meeting of the Madras State Forest Utilisation Advisory Board held in the first week of May, 1959, at Ooty and also visited the wattle plantations in the Nilgiris.

The following practical demonstrations carried out under the Extension Service Programme of the Institute have been completed:

- (1) Madras Tanage of Cow Hides at Government Tanning Centre, Anjad (M.P.).
- (2) Manufacture of (a) Madras Tanned Hides (Cows), (b) Kattai leathers; (c) Improved colouring methods of vegetable tanned leathers, and d) simple chrome tanning for charas, at Tanners' Colony, Rewari, Punjab.
- (3) Improved Bag Tanning at Khadi Board Tannery, Bassi or Sanganeer, Rajasthan.
- (4) Improved Bag Tanning Process at Tanners' Colony, Abu Road, Rajasthan.

Mr. V. Radhananda Kishore, J.S.A., has been awarded the M.Sc. Degree of the Madras University. The title of his thesis submitted in partial requirements of this degree, is "Studies on sulphated oil products and their application to leather".

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

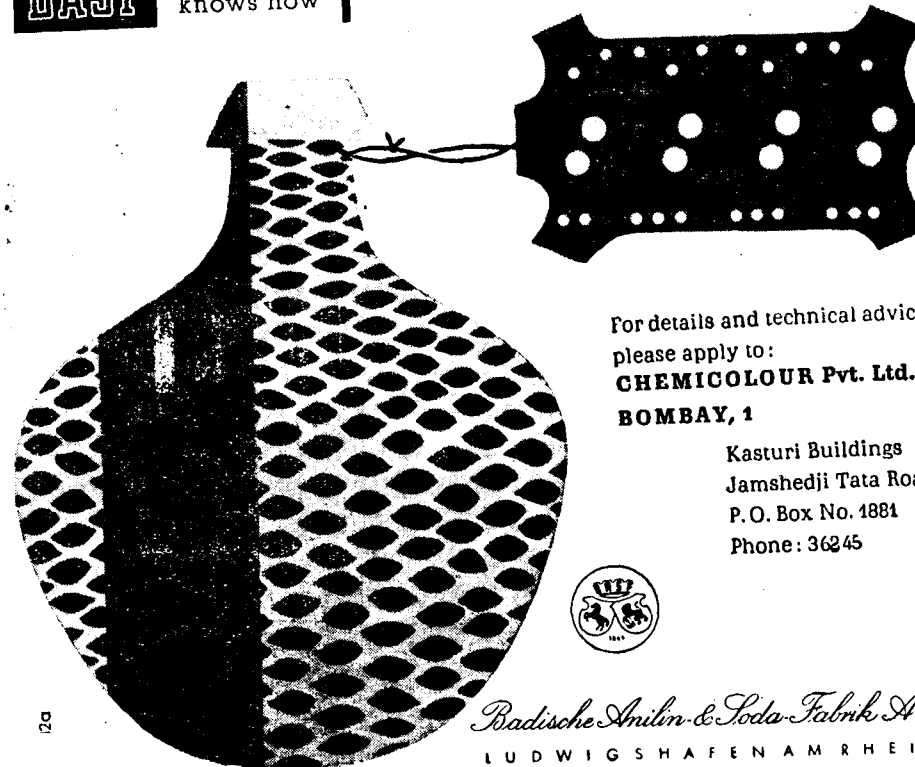


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