UTILIZATION OF INDIGENOUS TANNING MATERIALS.

PART I. MANUFACTURE OF TANNIN EXTRACT FROM AVARAM BARK (*CASSIA AURICULATA*, LINN).

By Keshaviah Aswath Narain Rao and Shaha L. Janniah.

Avaram bark, also known as Turwad, Turwar, Avla, Thangadi and Tanner's Cassia, is the most important tan-bark of South India. It is obtained from *Cassia auriculata*, Linn., a bush which grows wild in the South and West of India, covering large areas in the Deccan. It is also found in the dry zone of upper Burma. The right of collecting the bark from Government forests in India has for years been granted on contract, usually put up to auction, by the Forest Department. The bark is, however, much more plentiful outside reserve forests, occurring on most village lands. The method of collection consists in cutting off at the base, branches and twigs which spring from the roots. The coppiced bush sends out a large number of shoots, and a new harvest can be taken after a year.

The use of the bark is more or less confined to Southern India, where in the past, it was the principal material for tanning hides and sheep and goat skins. The amount of bark collected in Madras provides only a part of the local requirements, two-thirds of the total quantity employed being obtained from Mysore and Hyderabad. In Mysore, it is found in abundance in all the Maidan Districts and in the Maidan Taluks of the Malnad. Though information as to the actual quantity of bark collected annually is not easily available on account of collection being done by contractors, the quantity annually disposed of is estimated at 11,000 tons (1914–1915). The income from this tan-bark formed a large percentage of the revenue from minor forest products; an amount of Rs. 2,80,700 was realised in 1914–15 (*Commercial Guide to the Forest Economic Products of Mysore*, 1917, pp. 136–137). The value of the bark can be better realised when it is mentioned that the bark exported from the State during 1927–28 and 1928–29 was respectively 1,68,000 maunds and 2,28,000 maunds, valued at Rs. 10·24 lakhs and Rs. 13·24 lakhs.

The history of the Avaram bark tanning industry underwent a serious change after the year 1915. It was just at this period that the Wattle bark industry in South Africa developed considerably, resulting in large exports of Wattle bark and extract and that, at a very low cost. The effect of this can be realised from the figures of the Indian Official Returns (*Bulletin of the Imperial Institute*, "*Tanning Materials*

of the British Empire," 1929, p. 22). While the import of Natal bark was 25,952 cwts. during 1915–16, it was 176,615 cwts. during 1927–28.

The South Indian tanners found, on a comparative basis, that Wattle-tanned hides weighed more than Avaram-tanned ones. Since the South Indian tanned hides are sold by weight, instead of by area, this presented an attractive feature to the tanners. Moreover the weight of Wattle bark required for tanning a quantity of hide was only half that of Avaram bark required; this is due to the high tannin-content of Wattle. Wattle is an astringent catechol tannin, lending itself particularly to sole-leather manufacture; but it can also be used very successfully for making light leather, and the colour of the leather is much lighter (and much less affected by exposure) than that obtained from many other catechol tannins. It also makes a very good blend with acid-producing tanning materials, such as Myrobalams, yielding a firm and durable leather.

Further, during the war, the enormous demand for Avaram bark, consequent upon the necessity for increased output of the South Indian tanneries, caused many areas to be stripped in such a way that the supply was seriously affected and great anxiety was manifested as to the renewal of regular supplies. The usual price of Avaram was about Rs. 45 per baram of 500 lbs. which jumped during the war to Rs. 100 per baram. The export of Wattle bark to Germany and England having ceased during this period, this bark was forced on the Indian Market. At first, very few tanneries in Bangalore took to it; but due to various causes, the price steadily dropped from £ 20 to £ 9–10–0 per ton.

The present market rate of Avaram is Rs. 25 a baram. The price obtained for the tanned hides does not permit its use at such a high cost, as the principal tanning agent. The local bark can be used in preference to Wattle only if Avaram is sold at Rs. 15 or less a baram. The matter is more serious now on account of the abolition of import duty on Wattle from April 1930.

In spite of these considerations most tanners still prefer to use Avaram for tanning sheep and goat skins for which it is still the best tanning material. Indeed, the success of the tanning industry in South India is regarded as almost entirely due to the peculiar qualities of Avaram, which is excellent for manufacturing certain types of leather.

Under these circumstances, the question of making available to the tanners, the tannin in Avaram at an economical price has been seriously taken up. The possibility of manufacturing a satisfactory tannin extract in the locality where the bark is available and supplying it to the tanners at Bangalore has been investigated in the first instance.

The advantages of extracts over the raw materials are many. A high percentage of tannins is offered to the tanners in a small bulk and transport charges are lowered considerably; at least 90–95 per cent. of the tannins in the raw material is made available to the tanner; and all the tannins being in a readily soluble form, the period of tanning is considerably reduced. Moreover, the tanner is assured of the supply of a material of uniform quality, instead of a bark each piece of which varies in its tannin-content. The most important condition is that the extract should retain all the good characteristics of the raw material.

EXPERIMENTAL.

This Indian tanning material has been the subject of extensive investigations by Limaye, Mehd and Fraymonth, and Pilgrim. It is also mentioned in the earlier reports on the Indian Leather Trade by Guthrie and Chatterton.

Tannin content.—The tannin-content of Avaram bark varies from 12 to 18 per cent., though samples containing 20 and 23 per cent. have been mentioned (*The Bulletin of the Imperial Institute*, "*Tanning Materials of the British Empire*", 1929). In order to have an idea of the tannin-content of the samples of bark from different parts of the State, a collection of about 2,000 lbs. was made. The analyses carried out on these samples are tabulated below:

TABLE I.

Calculated to 10% moisture.

Sample	Percentages	
	Tans	Non-tans
From Peenya Plantation (Yeswantpur, Bangalore District)	15·0	11·3
From Srinivasapur (Kolar District)	18·0	10·6
Mixed sample (from Bangalore, Kolar and Tumkur Districts)	13·3	17·9
From Local Tannery	12·3	13·6

(All the tannin estimations in this work were done by the Hide Powder method, as prescribed by the I. L. T. A.)

It is seen from the figures given above, that though individual samples may contain tannins from 15 to 18 per cent. and have the ratio of Tans/Non-tans greater than one, the tanners obtain rather

poor grades of bark containing only 12 to 13 per cent. tannins, with the ratio, tans/non-tans very often less than one.

The tannin-content depends very much on the age, and the parts of the plant cut. The former has been clearly pointed out by Seshachalam Choudary and Yoganandam ("Studies in Avaram Bark" 1, *Jour. Int. Soc. L.T.C.*, 1928, **12**, 55-58) who found that tannin-content varied from 15·58 per cent. in a shrub one year old to 19·06 per cent. in one of 6 years. They came to the conclusion that it was best to collect the bark from plants five years old. Also, the bark taken from the lower part of the plant is usually richer in tannin than that taken from the upper parts. Linaye (Harvey, *Tanning Materials*, p. 92) found a difference of 1–1·5 per cent. between the lower and upper parts of a plant.

But the above two considerations are rarely taken into account by the contractors who collect the bark and hence the supply of poor grade of bark to the tanners.

Extraction.—The tannin present in Avaram belongs to the catechol group and is fairly easily extracted by water. The temperature of water for extraction has been worked out by Mehd and later, by Seshachalam Choudary and Yoganandam (*loc. cit.*), who found that the maximum percentage of tannins was extracted at 95°–100°, and thus concluded this range to be the optimum temperature for extraction of Avaram bark. The preliminary experiments carried out in the present investigation confirmed these results.

About 300 lbs. of bark were extracted with water between 95°–100°C. by the open-vat system. The leaching tanks were made of copper, each measuring about 22″ in diameter and 23″ in height, capable of holding about 50 lbs. of crushed bark together with about 20 gallons of water. They were also fitted with outlet taps very near the bottom on the side, and in order to prevent the taps being choked up by the crushed bark, a perforated false bottom was placed inside the vessel about 2″ from the bottom. Heating was done by steam, and as copper tubes are expensive, lead tubes (5/8″ diameter, 34′ in each tank) were used instead and were quite satisfactory. It was found in practice that the liquor could be heated up to 95°C. in about 15 minutes. A battery of four such vats was arranged and each charge of water worked through the whole series in such a way that stronger liquors passed through fresher bark, yielding in the end a fairly concentrated liquor. Six leachings, each extending to about 20 minutes, were found necessary to exhaust each charge of bark. The warm liquors were drawn out through the outlets and were fairly clear having been filtered through the column of the bark. But while attempting further clarification by sedimentation, it was observed that a good quantity of solid deposited at the bottom of the vessel and was found to contain some tannin. This must

have been the difficultly soluble tannin which separated out on cooling the liquor.

But it was observed that the liquor thus obtained was particularly dark in colour. This was surprising in view of the experiments of Seshachalam Choudary and Yoganandam (*loc. cit.*). Their figures indicate that the colour is maximum when extraction is carried out at lower temperatures and is much lighter at higher temperatures.

Further preliminary experiments carried out, in order to find the best conditions for getting light-coloured liquor, suggested the employment of lower temperatures for the extraction of the major portion of the tannin, heating the fresh water to about 95°C. being resorted to only to extract the last portions of tannin. These results are in entire agreement with the statements made by Wilson (*Chemistry of Leather Manufacture*, Vol. 1, pp. 409–415): "The rate at which tannin can be extracted from the raw material increases with the temperature of the water used, but so also does the rate at which the dissolved matter decomposes. It is customary to extract the fresh material at a low temperature and to increase the temperature of extraction until the material is practically exhausted. In using the open-vat system for ordinary barks, it is a good plan to have the fresh water at the boiling point and to allow its temperature to fall slowly to about 60°C. as it passes over the fresher bark." This prevents to a certain extent the decomposition of tannin and darkening of colour of the liquor.

The method of extraction was, therefore, modified. The successive extractions were carried out with water at temperatures of 50°, 60°, 70°, 80°, 90° C. and finally with boiling water. The time of leaching also ranged from one hour for the first leaching to about quarter of an hour with boiling water. By this modification, the amount of extracted matter (as determined by the total soluble solids in the liquor) amounted to roughly 95 per cent. of extractable matter in the bark as against only 80 per cent. extraction by the previous method. There was decided improvement in the colour of the liquor.

Even this liquor when concentrated as described later and used for tanning did not give satisfactory results. Besides the control of the temperatures in the different stages of extraction, the one other factor in extraction, which affects the colour of the liquor, is the pH value of the water. The work of Wilson and Kern (*Chemistry of Leather Manufacture*, Vol. 1, pp. 409–415) has shown that acidified water with a pH value of 5 is better than ordinary water inasmuch as it prevents the oxidation of the tannin effectively; and moreover, tannins are not precipitated by lime when water with a pH value below 7 is used. Water acidified with acetic acid was, therefore, used for extraction, with some beneficial result.

Decolourisation.—The necessity of improving the colour further was evident. A number of materials like Fuller's earth, kaolin, alum, aluminium sulphate (alone and in conjunction with oxalic acid), soluble albumin, borax, etc., were tried without any appreciable effect. A saturated solution of sulphur dioxide gave better results. To the warm, turbid tan liquor from the leaching tanks, sulphurous acid was added in small quantities at a time with constant stirring, till there was a faint smell of sulphur dioxide. The liquor was stirred for another quarter of an hour and allowed to settle. The quantity of sulphurous acid required varies with concentration, temparature, etc., of the liquor, but usually 200-350 c.c. of a saturated solution for every 50 gallons of tan liquor were found sufficient. It is well known that sulphur dioxide not only lightens the colour of the liquor, but also helps the dissolution of the difficultly soluble tannins which otherwise would be lost by precipitation. In illustration, an extract liquor in which the ratio, tans/non-tans was 6·8/8·9, *i.e.*, <1, after being treated with sulphur dioxide, analysed to 9·7/5·2, *i.e.*, >1. In the untreated extract liquors, a considerable quantity of tannin is lost by precipitation during clarification, and this loss is prevented by sulphur dioxide.

The growth of molds in tan liquors is very common when kept even for two or three days. It is, therefore, usual to employ inhibitors like thymol, phenol, formic acid, etc. In the present investigation, it was noticed that sulphur dioxide itself prevented the growth of molds effectively and no other inhibitor was found necessary.

It may be mentioned that a solution of sulphur dioxide was used in preference to sodium bisulphite as the effect of the latter was found to be more of solubilising than of decolourising.

Concentration.—From the laboratory experiments carried out in the present work, it was found that a solid extract analysing to: tannins 45 per cent., non-tannins 23 per cent., insolubles 13 per cent. and water 19 per cent., was not quite satisfactory, the percentage of insolubles being too high. Besides, it was not readily soluble in cold water; hard lumps or cakes were formed when the extract was mixed with water and dissolution was slow even with agitation. It was, therefore, decided to concentrate the liquor to a soft extract.

The apparatus employed was the Laboratory Vacuum Film Evaporator described by Watson (*J. Indian Inst. Sci.*, 1919, **2**, pp. 209-212). The effective length of the tube was 12 ft. and the separator measured 6″ x 8″; the helical beffle was found unnecessary. The evaporative capacity of the tube was 10-15 litres of water per hour under a pressure of 100-200 mm. of mercury, using steam at 25-30 lbs. pressure.

From the preliminary experiments with this evaporator, it was found convenient to concentrate the liquor to a soft extract in two stages instead of one. The first stage consisted in concentrating the

tan liquor roughly from 5 to 1 by volume. This gave a fairly thick liquid which analysed to : tannins 19·0 per cent., non-tannins 14·5 per cent., insolubles 2·5 per cent. and water 64·0 per cent. This was again fed into the evaporator and further concentrated to an extract, which, while warm, was sufficiently mobile to flow from the separator into the receiver. The ratio of extract to water distilling off in this second stage was approximately 1 : 3 by volume. The average sample of the soft extract obtained was analysed and found to contain tannins 35 per cent., non-tannins 28 per cent., insolubles 3 per cent. and water 34 per cent. In later experiments, it was found possible by further concentration to obtain extracts having a tannin-content of 38 per cent.

Tanning.—The tanning was carried out in the local tannery by the tanners and the process of tanning was similar to the one in use in bark-tanning.

It is customary to carry out tanning with Avaram bark in three stages, each for a period of 7-8 days; a final finish with myrobalams is then given. The same method was adopted with the extract also. The quantity of extract employed in each stage was corresponding to the amount of tannins made use of, from each charge of bark. From the following figures,

		Tannins	Non-tannins
Fresh Avaram bark	..	11·8	13·1
Spent Avaram bark	..	5·6	9·7

it will be seen that only about half the quantity of tannins contained in the bark is made use of, the rest being wasted in the "spent" bark. This available percentage of tannins is higher the better the quality of bark employed. By knowing the quantity of bark employed in each stage, the amount of tannins actually used up was calculated and the quantity of extract to be used was determined from these data.

The extract prepared from liquors when leaching was carried out at 95°–100°C., produced very dark-coloured leather. There was no doubt that the extract was quite unsuitable if colour, a very important factor indeed, is taken into account. An extract by the modified method was found to yield leather of a decidedly lighter shade. But even this was not quite satisfactory; the leather was still red which would certainly darken on exposure. It is expected, however, that the extract prepared from liquors treated with sulphur dioxide would produce leather of a suitable quality.

It was found that, while a period of 22 days is usually required for Avaram bark tanning, the whole process was complete in 13–14 days when extract was used.

Discussion.—There are a number of factors which cause this darkening of the colour of leather. Firstly, the work of Wilson and Kern ("The Colour Value of a tan liquor as a function of pH,"

Ind. Eng. Chem., 1921, **13**, p. 1025) has proved beyond doubt that the colour of tan liquor, and consequently of leather, depends largely on the pH value of the liquor. It should be maintained as low as possible, usually in the neighbourhood of 4. Increase in the pH value of the liquor while tanning is going on must be checked either by added acids or substances which form acids. In this respect the raw materials have a decided advantage over the extracts. They contain more or less quantities of fermentable sugars—the quantity varying with different materials—which produce acidic substances while the tanning proceeds. This automatically maintains the acidity of the liquors in the vats fairly steady. In the case of extracts, on the other hand, these sugars are destroyed during concentration of the liquors and the pH value of the liquor increases very rapidly thereby affecting the colour of the leather seriously. It is hoped to prevent this destruction of acid-producing materials in future experiments.

TABLE II.

Avaram Extract.

		pH value
Fresh liquor	..	4·4
After 1 day	..	4·6
„ 2 days	..	4·8
„ 3 „	..	5·6

Before tanning experiments were done, day-to-day analyses of the vat liquors of Avaram bark, and incidentally of Wattle bark also were carried out in order to be able to carry out extract-tanning under similar conditions.

TABLE III.

Avaram Bark Liquors.

Time	pH	Percentages		
		Sol. Solids	Non-tans	Tannins
Fresh liquor ready for use ..	4·4	1·9	0·9	1·0
With leather for 1 day ..	4·5	1·5	1·0	0·5
„ „ 2 days ..	4·6	1·4	1·2	0·2
„ „ 3 „ ..	4·6	1·3	1·2	0·1
„ „ 4 „ ..	4·6	1·4	1·2	0·2
„ „ 5 „ ..	4·6	1·3	1·3	0·0
„ „ 6 „ ..	4·7	1·2	0·9	0·2
„ „ 7 „ ..	4·7	1·1	0·7	0·4
„ „ 8 „ ..	4·6	1·1	0·5	0·7
Spent liquor	4·6	1·0	0·8	0·2
2nd stage tan liquor ..	4·4	1·4	0·8	0·5
„ „ for 10 days ..	4·4	1·3	1·0	0·3
„ „ „ 11 „ ..	4·6	1·3	1·0	0·2

TABLE IV.

Wattle Bark Liquors.

Time	pH	Percentages		
		Sol. Solids	Non-tans	Tannins
Tan liquor for fresh leather: fresh water *plus* spent liquor with bark for 24 hours ..	4·4	1·7	0·8	0.9
After 1 day with skin ..	4·5	1·6	0·9	0·7
„ 2 days ..	4·7	1·7	1·1	0·6
„ 3 „ ..	4·7	1·5	1·2	0·3
„ 4 „ ..	4·7	1·4	1·0	0·4
„ 5 „ ..	4·9	1·3	1·1	0·2
„ 6 „ ..	5·2	1·7	1·2	0·5
„ 7 „ ..	5·0	1·3	1·1	0·2
„ 8 „ ..	5·4	1·2	1·2	0·0
Spent liquor ..	5·2	1·3	1·1	0·2
Fresh bark after 1 day ..	4·4	0·9	0·4	0·5
After 10 days ..	4·7	1·5	0·8	0·6
„ 11 „ ..	4·4	1·4	0·7	0·7
„ 12 „ ..	4·4	1·1	0·8	0·5
„ 13 „ ..	4·4	1·1	0·8	0·3

From the above two tables, it is clear that the pH value increases slowly from 4·4 to 4·7 (in the case of Avaram) and from 4·4 to 5·4 (in the case of Wattle) during the period of a week. This is certainly slow compared with the rate of increase in extract liquors (Table II).

The addition of suitable acids or acid-forming substances to the extract or to the extract liquors is, therefore, a matter of necessity. The first alternative which suggests itself is the preparation of mixed extracts from Avaram and other suitable tanning agents.

Secondly, the method and rate at which the tanning proceeds seems to be another factor affecting the colour and softness of the leather. From Tables III and IV, it is clear that the concentration of tannin in the vat liquor is rarely more than 1 per cent. Since cold water can extract the tannins from the raw material only very slowly, small quantities of tannins are available, at any given time, for the hides to absorb. In the case of extracts, all the tannin is in a readily soluble form. The rate at which tannins penetrate into the pores of the hides is, therefore, very much greater than the rate at which they form insoluble hide-tan substances. This results in some tannin being merely mechanically held in the pores of hide and therefore easily oxidised, changing thereby the colour of the leather to a darker shade.

The leather, produced by rapid tanning, was also much harder than ordinary bark-tanned leather.

CONCLUSION.

In view of these considerations and experimental results, it looks improbable that Avaram extract alone is suitable for tanning, particularly by the old-fashioned methods prevalent in our tanneries. Mixed extracts will be prepared and tried. There are a number of tanning agents like Myrobalams, Divi-divi, *Cassia fistula*, and *Anogeissus latifolia*, fairly rich in sugars and which, besides, are known to produce light coloured leathers (due to the nature of tannins present). It is proposed to use these materials in conjunction with Avaram extract or even extracts of these materials with Avaram extract. Also, it is absolutely necessary to work out the method of using these extracts, since any slight variation in the process of tanning with them is likely to yield bad results. It is proposed to continue the work in the direction mentioned above.

SUMMARY.

Extract of Avaram has been prepared on a semi-commercial scale and used in local tanneries. It has been found fairly satisfactory, except for one or two defects, which it is hoped to overcome.

Useful data on the changes occurring in the vat-liquor during tanning have been collected and recorded.

This work was done for the Government of Mysore, whom we wish to thank for granting scholarships to both of us. In conclusion, we have great pleasure in thanking Dr. H. E. Watson for his kind interest in this investigation and Mr. B. V. Ramiengar, Chief Conservator of Forests, for placing at our disposal the resources of his Department and for advice.

Department of General & Organic Chemistry,
Indian Institute of Science,
Bangalore.

[Accepted, 5–8–1934.]

P391-34.—Printed at The Bangalore Press, Mysore Road, Bangalore City, by T. Subramania Aiyar, Superintendent.