PRACTICE OF 'BLENDING' FOR THE MANUFACTURE OF VEGETABLE TANNED LEATHER

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Vegetable tannins are a group of similar astringent substances, which are complex organic compounds of the aromatic series of high molecular weight. They would normally be insoluble in water but for the presence of lyophilic groups. Tanning takes place because of the reaction of the polyphenolic substances with the reactive groups of collagen. The cross linking of collagen by multivalent tannin molecules confers the necessary structural stability to the tanned hide or skin.

The process of tanning is one of the earliest crafts known to mankind and in all probabilities, vegetable tanning was the earliest form of tanning to be practised. Bark tanning was known more than 12,000 years ago according to the famous German archaeologist Dr. Watter Vonstoekar. Vegetable tanning is the most natural method of tanning, requiring minimum control in its operations. The skill associated with this craft was handed down from generation to generation. Vegetable tanning is practised extensively in all parts of India where we have got a primarily village-based economy and the part played by vegetable tannins, in our internal and export economy is considerable.

Vegetable tannins may be broadly classified as hydrolysable tannins and condensed tannins. The former on hydrolysis with acids, alkalis or enzymes yield glucose and gallic or ellagic acids. The phenolic residues are linked to sugar radicals through oxygen atoms. They are usually quite acidic, contain fairly large amount of sugars and are better buffered. They deposit bloom due to the action of enzymes. Condensed tannins are not hydrolysable and by condensation yield 'phlobaphenes' in acid medium. Here the phenolic radicals are linked to each other via carbon atoms. They contain very little acids or sugars and are very sensitive to pH.

In the actual practice of vegetable tanning, for the manufacture of a variety of leathers, the major share of which forms heavy leather tanning, a mixture of tanning materials is used. This judicious admixture is known as "blending" in tanners' parlance. The object of blending is manifold and may be summarised as follows :

(i) Tanning materials of high T/N. T. ratio, for eg. quebracho, are very astringent. By blending with mellow tanning materials, the astringency can be adjusted to the optimum requirement of tannage, as otherwise a harsh leather will result. There will be overtanning on the grain and the tanning as a whole will not be uniform through the cross section of the pelt.

(ii) Catechol tanning materials have normally a higher pH. While this factor is conducive to penetration of tannins into the pelt, there will not be sufficient fixation at higher pH levels. To avoid this defect, catechol tanning materials like wattle or quebracho are usually blended with pyrogallol materials like chestnut or myrobalan.

(iii) Materials like myrobalan, hydrolyse giving copious deposition of bloom. This aids in giving weight and solidity to the leather, in sole leather manufacture. Hence with most of the sole leather tanning procedures, blending with myrobalan is a very common practice. In western countries, chestnut, oak bark and valonea are used mostly, though myrobalan is also used occasionally.

(iv) Vegetable tannins are complex organic substances and hence each tanning material has a distinctive peculiarity. Each material imparts its particular characteristics like colour, feel, fullness, smoothness of the grain, tearing strength etc. So when the manufacturer aims at specific requirements in the final leather, he will have to blend two or three suitable tanning materials to achieve his object.

(v) During the actual tanning procedure, factors like molecular weight, particle size, acid-salt ratio, surface tension, viscosity, etc ; of the materials used, exert pronounced influence on the tannage. Hence blending assumes very great importance in as much as to achieve the desired objectives, two or three materials will have to be blended. Especially for rapid tanning of hides,[2] tanning mixtures of low viscosity, medium astringency and low salt content are required.

(vi) Sometimes, blending is resorted to, for reasons of economy. It is not uncommon to use cheaper materials within reasonable proportion to effect a saving in the costlier tan materials. For instance, for E.I. kips, it was a usual practice to mix konnam with avaram. Similarly, mixtures of two or three materials have been traditionally in use, in the villages of India for vegetable tanning.

In western countries, the vegetable tanning materials used predominantly are wattle, quebracho and chestnut while oak, valonea, sumac, algarobilla etc. are used to some extent. In recent times, tannage with wattle alone has become quite common.[4] Blending with syntans or pretanning with syntans are also practised. The most common blends are quebracho-chestnut, wattle-myrobalan and quebracho-myroblan. For rapid tanning, suitable blends from wattle, quebracho, chestnut and oakwood extracts with or without syntans are used. Certain usual blends are given below :

1.	Quebracho extract	75%	on tannin basis
	Myrobalan ,,	25%	
2.	Wattle ,,	75%	
	Myrobalan ,,	25%	
3.	Wattle extract	40%	on material basis
	Quebracho extract	20%	
	Chestnut ,,	20%	
	Syntan	20%	
4.	Chestnut extract	50%	on material basis
	Sweetened chestnut	30%	
	Quebracho extract	20%	
5.	Oakwood extract	60%	on material basis
	Syntans	40%	
6.	Oakwood extract	45%	on material basis
	Willow bark extract	45%	
	Syntans	40%	
7.	Sulfited quebracho	20%	on material basis
	Wattle extract	10%	
	Chestnut	5%	
	Spruce bark extract	25%	
	Syntan	40%	

The blends used above are mainly for sole and heavy leathers. For skins, blends of sumac, gambier, algarobilla etc. are used. However, it may be mentioned that the manufacture of vegetable tanned skins is negligible in foreign countries, since they depend mainly on imports from developing countries.

In India, the most common blends are wattle-myrobalan and babul-myrobalan. Probably one of the earliest blends was avaram-konnam used for E.I. kips. From the literature available on vegetable tanning many formulae for blending are found and some of the interesting mixtures are quoted below :

1. Babul bark 1 part
   Goran bark 1 part
   Myrobalan nuts 1 part
   } on tannin basis

2. Wattle bark 4 parts
   Myrobalan nuts 1 part
   } on material basis

This mixture can be used in the leach battery also.

In sole leather tanneries of Kanpur, one part of babul and one part of myrobalan are leached together and the liquor is strengthened with one part of wattle extract.

In Calcutta tanneries, the blend commonly used is

Wattle extract	3 parts
Myrobalan extract	1 part

3. For quick drum tanning of V. T. sole :

   Quebracho extract 75%
   Myrobalan extract 25%
   } on tannin basis

4. For bag tanning :

   Babul bark 10 parts
   Myrobalan nuts 1 part
   } on material basis

In Punjab, sometimes babul alone is used for bag tanning.

5. For heavy leathers :

Goran	2 parts	Goran	1 part
Babul	1 part or	Babul	2 parts
Myrob	1 part	Myrob	1 part

(on tannin basis)

In recent researches at Central Leather Research Institute, modified mangrove extract and modified cutch extract[6] along with babul and myrobalan have been successfully utilised for sole leather tanning as follows :

1. Mod. mangrove extract 1 part
   Babul bark 1 part
   Myrob nuts 1 part
   } on tannin basis

2. Mod. cutch extract 1 part
   Babul bark 1 part
   Myrob nuts 1 part
   } on tannin basis

In some of the earliest records, the following blends are found.[7] The blends 1 - 7 are mainly used for tanning cow hides, while the mixtures 8 - 10 are for E.I skins and kips.

1. Dhawa leaves 25%
   Dhawa twig bark 25%
   Anola bark 25%
   Mahurain (*Bahunia vahlii*) 25%
   } on material basis

2. Avaram bark 50%
   Konnam bark 50%
   } on material basis for E.I. kip

3. Babul bark 60%
   Dhawa leaves 20%
   Ghat bor nuts 20%
   } on material basis

4. Ghat bor 25%
   Karaunda leaves 25%
   Sal bark 15%
   Anola twig bark 15%
   } on material basis

5. Karaunda leaves 1 part
   Babul bark 1 part
   Ghat bor 1 part
   } on material basis

6. Dhawa twig bark 10%
   Dhawa leaves 20%
   Goran bark 25%
   Ghat bor 25%
   Karaunda leaves 20%
   } on material basis

7. Goran bark 15%
Sundri bark 20%
Dhawa twig bark 15%
Ghat bor 30%
} on material basis

8. Wattle mixtures for half tan or E.I. :

Avaram bark 45%
Wattle bark 35%
Dhawa leaves 20%
} on material basis

9. Wattle bark 50%
Dhawa leaves 25%
Sumac 25%
} on material basis

10. Avaram bark 33.3%
Gothor fruits 66.6%
} on material basis

There are many other blends used in the villages of India depending upon the local availability. Mixtures of sam, sal, arjun, karada and many other locally available materials, common and uncommon, are blended with babul and myrobalan successfully.

Recently a process was developed for the manufacture of sole leather using a blend of wattle extract and tamarind seed husk[9].

In the context of "blending", it will be appropriate to highlight the work done in CLRI during the last two decades. For the purpose of substituting wattle bark and promoting the use of relatively less known tanning materials, considerable work has been done and several blends or tanning mixtures have been formulated by the research workers from time to time. Kedlaya *et al*[11] have given exhaustive data on various indigenous tan materials and blends in the 'Assessement of Indian tanning materials'.

Rao *et al*[12] in their attempts to find substitutes for wattle bark, formulated the following blends :

1) Goran bark and dhawa leaves, 1 : 1
2) Karada bark and dhawa leaves, 1 : 1
} for kips

3) Konnam bark and dhawa leaves, 3 : 1 — for E.I. skin and kips.

Selvarangan *et al*[13] tanned E. I. kips using iron wood of Malabar (*Hopea parviflora*) in the following blends :

Process No. I. Two bark

1st bark :

Hopea bark 100%
Konnam bark 37.5%
% on expected yield of leather

2nd bark :

Same as above

Process No. II Single bark

Hopea bark 100%
Myrobalan nuts 17.5%
Wattle extract 25%

For E. I. tanned goat, sheep and cow hides, Krishnan, *et al*[14] used a blend of konnam, babul, wattle bark and wattle extract in suitable proportions to yield 16% tannins on fleshed weight. Rajabather[15] formulated two blends of karada and konnam, and babul and karada for tanning E.I. kips.

While investigating the possibilities of new barks for E.I. tanning, Varma *et al*[16] successfully found out the following blends for tanning cow hides.

Peltophorum bark and myrobalan nuts 6 : 1

Peltophorum bark and Pithecolobium bark 1 : 1

Peltophorum bark + Pithecolobium bark + Myrobalan nuts 3 : 3 : 1

For sole leather tanning, Ganesan and Vijayaramayya[17] have successfully tried a blend of babul and myrobalan, suitably

strengthened with wattle extract. For bag tanned sole leather, Sovani and Ganesan[15] have tried Aain bark and myrobalan nuts in the ratio 2 : 1. Sovani *et al*[17] have also tried Ghat bor and myrobalan (3 : 1) for tanning cow hides. Muthiah *et al*[20] have used a blend of wattle extract and myrobalan extract in the ratio 3 : 1 for sole leather, while almost the same recipe is used by Mahadevan and Venkatachalam[21] for cycle saddle leather.

For rapid E.I. tanning[22] of hides and skins, a blend of avaram and wattle extract has been used, the quantities being avaram bark 100% and mimosa 40% on expected yield. For book binding[23] leather a workable blend is formulated with myrobalan and wattle (8 : 1) with a suitable buffer solution.

Recently an improved method of E.I. tanning[24] using a blend of avaram and konnam has been developed. The tanning materials used are as follows :

1st bark :

Avaram	35%	on pelt weight
Konnam	35%	

2nd bark :

Same as above

Projects on blended extracts may thoretically appear to be very sound and viable but there have been many handicaps which are yet to be completely eliminated. No doubt, we have blended extracts like Wasub and Wasub super in the market now and blends with cashew testa are on the way. In fact, Procter[9] was a very strong advocate of blended extracts and Puran Singh[10] gave vehement support to his theory. The latter went as far as to postulate that in tropical countries like India, blended extracts will prove the real answer. But in spite of vigorous efforts during the last several decades, the proposition of blended extracts has not caught the fancy of the tanners. One reason might be that the tanner would find it easier to make a blend suited to his requirement from the individual materials instead of a ready made blend whose composition he is not sure about. Another reason may be that the blended extracts do not necessarily keep in tact the inherent qualities of the constituents.

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