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PRELIMINARY INVESTIGATIONS ON THE EFFECTS OF NAPHTHALENE - BASED SYNTAN ON ACCACIA NILOTICA TANNING MATERIAL

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ABSTRACT

Modification characteristics of *Accacia nilotica* (Bagaruwa in Hausa) vegetable tanning material with naphthalene–based synthan have been investigated. The initial results showed that blending at a total concentration of 60% W/W Bagaruwa/Syntan ratios produced some synergisms such as improved colour, antimould activity, higher hydrothermal stability and increased rate of penetration of Bagaruwa tannins, hitherto lacking in the individual tanning materials. However, greater synergisms were displayed by the blends at 30:30% W/W and 20:40% W/W Bagaruwa/syntan ratios.

Key words: Syntan, Synergism, Shrinkage Temperature, Blooms, Mould growth.

INTRODUCTION

Nigeria has a large number of plant species which scientific tests have shown to contain exploitable tannins, for use in the tanning industry and possibly export to earn foreign exchange. These plant species include *Accacia nilotica* (28-30%) *Parkia Clapatoniana* (45%). *Magnifera indica* (20%), among others. (Theresa, 1979 – 80)

Accacia nilotica is the local vegetable tanning material use by tanning industries in Nigeria. The pods are greatly utilised for its higher tannin content.

Chemical analysis has shown that it contains both hydrolysable and condensable tannins, and with its natural pH of about 4.0 to 4.4 and a tan to non–tan ratio of 1.5:1, it displays unparallel suitable characteristics for tanning (Adewoye and Bangarswamy 1989). Therefore its preference among other plant species for the production of vegetable crust leathers for export may be anchored on these qualities. The recent ban on the exportation of wet–blue (chrome) leathers by the Federal Government of Nigeria, emphasis is now placed on the exportation of finished leathers, leather goods and vegetable crust leathers (Mustapha, 1996). The consequence of this is that there is growing demand for the usage of tannins extracted from Bagaruwa.

Ironically, the lack of necessary technology to produce the commercial extract forms of pure Bagaruwa tannins which are better and more economical, poses serious problems as most of the present day tannins produce contain solid wastes. Moreover, it has been known that vegetable tanning liquors generally develop sludges on standing, thus reducing their tanning potencies (Venkataboopathy et al., 1981). Sludge formation is more prevalent with Bagaruwa because of the presence of both hydrolysable and condensable tannins mentioned above. In addition, Sludge formation especially blooms encourages mould growth on the resultant leathers during storage (Venkataboopathy et al, 1982).

However, recent attempts at developing a standard method for the production of tannins from Bagaruwa pods is still in the experimental stages with little or no promising results (Mustapha 1996). This research therefore aims at investigating the chemical modification of Bagaruwa tannins with various concentrations of naphthalene–based syntan (synthetic tanning material) to ascertain its tanning potency against the backdrop of the aforementioned problems.

EXPERIMENTAL

Raw Materials and Reagents.

7 pieces of wet–salted goatskins were obtained from samaru. Bagaruwa pods were obtained in Zaria. Naphthalene–based syntan with trade name paralene PGS manufactured by Yorkshire Chemicals, U.K. was obtained from Arewa Tanneries, Kano, Nigeria. Other industrial grade chemicals include NaCl, Na_2S, hydrated lime $Ca(OH)_2$, $(NH_4)_2SO4$, $NaHCO_3$, Sulphated fatliquor (oil-in- water emulsion).

Laboratory grade reagents include: Phenolphthalein indicator, methyl Orange indicator, formic acid, and sulphuric acid.

METHOD

Bagaruwa pods were ground and sieved to fine powder. The powder was analysed for its

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moisture content, total ash, total solid, total solubles, tans, non – tans and pH of infusion using the methods of the Netherland Normalisation Organisation (TNO) and the Society of Leather Technologists and Chemists (SLTC).

PRETANNING PROCESSES

Soaking / Draining:

The skins were thoroughly washed to remove blood stains and dirts before soaking for 40 minutes. They were subsequently drained for about 20 minutes.

Pulping unhairing

The mixture of 3%W/W Sodium sulphide, and 3%W/W lime was dissolved in water to give a colloidal suspension, and the skins were then introduced and agitated for 30 minutes in a drum (6 rpm). The drum was left stationary for 2 hrs after which it was run again for 30 minutes. After pulping the skins were washed in clean water and drained.

Reliming

The skins were introduced into a solution of 4% W/W lime in 150% W/W water. They were left in the lime liquor for 24 hours to achieve swelling and plumping. The flesh on the plumped skins were subsequently removed on a fleshing machine to give the pure fibres.

Deliming

3%W/W $(NH_4)_2 SO_4$ was dissolved in 200 % W/W water. The fleshed skins were run in a drum (6rpm) until a cut edge gives colourless appearance with phenolphthalein indicator at pH 8.0 (this process removes lime both combined and uncombined, which would otherwise have detrimental effects on subsequent processes).

Drenching

A salt solution was prepared by dissolving 6% W/W NaCl in 60% W/W water. The pelts (skins) were then run in the salt solution for about 15 minutes. Then, 0.5% W/W HCOOH diluted 10 times its volume was added and subsequently run for 40 minutes. The pH was checked with methyl orange indicator to give pH of 4.4 (yellow) and the pH of the liquor confirmed on a pye Unicam, 292 MK2 pH meter tallied with that of the pelt. Drenching was carried out to lower the pH of the delimed pelts from 8.0 to that of the tanning liquor (4.0 – 4.5) for Bagaruwa infusion.

Sorting out and preparation of tanning blends

After drenching, the 7 pieces of skins (pelts) were sorted out and coded BS_1 – BS_7 corresponding to the various tanning blends. The percentages W/W Bagaruwa / syntan ratio for the blends were BS_1 (60:0), BS_2 (50:10), BS_3 (40:20), BS_4 (30:30), BS_5 (20:40), BS_6 (10:50), BS_7 (0:60) Note: BS_1 and BS_7 are full Bagaruwa and syntan respectively and percentages W/W are based on the weights of individual drenched pelts.

Tanning trials

To each of the tanning blends was added 150% W/W water based on the corresponding individual weights of the coded pelts BS_1 (200.0g); BS_2 (450.0g); BS_3 (350.0g); BS4 (400.0g); BS_5 (340.0g); BS_6 (300.0g); BS_7 (250.0g). The pH values of the tanning blend liquors where determined before the introduction of the coded pelts. Each trial was run, in a drum (6rpm) for 3hrs after which it was left stationary for 12 hrs. Thereafter, it was run again for 1hr. Again the pH values of the liquors after tanning were determined. The resultant leathers were washed and stored separately in polythene sheets. Meanwhile, shrinkage temperatures (Ts) of the various cut leather samples were determined on a shrinkage Temperature apparatus; (IUP/16). Furthermore, observations were made on the stored leathers on a daily basis for 4 days at the end of which they were washed in water, drained and spread to dry in shade preparative for fat liquoring process.

Fat liquoring

Fat liquoring is the treatment of leathers with oil-in-water emulsion in order to lubricate the fibres. Each tanned pelt (leather) was weighed as: BS_1 (1000.0g), BS_2 (225.0g), BS_3 (150.0g), BS_4 (200.0g), BS_5 (160.0g), BS_6 (150.0g), and BS_7 (160.0g). Each was soaked in 200% W/W to re-hydrate and thereafter drained.

The leathers were then separately stripped with solution of 0.75% W/W $NaHCO_3$ in 150% W/W water in a slow running drum (6rpm) for 20 minutes to raise the pH to about 5, which is the fat - liquoring pH, They were then drained and subsequently fat - liquored individually with 3% W/W sulphated fat liquor in 120% W/W warmed water at 40°C. Each sample was run in a drum for 45 minutes after which it was hung to dry. They were then conditioned (sprinkled with water) and toggle dried.

RESULTS AND DISCUSSION

Bagaruwa Tanning Analysis.

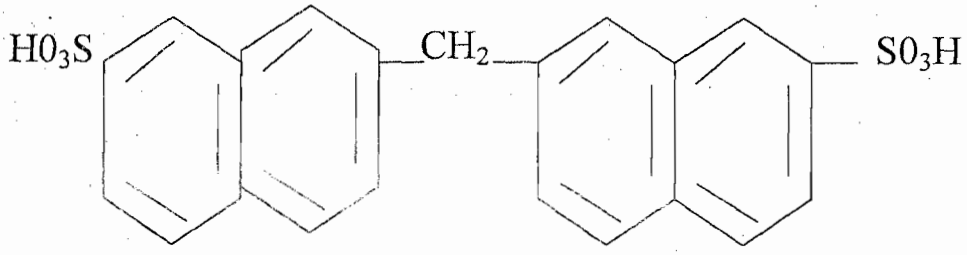
Tannin analysis indicated a moisture content of 13.3% at 102± 2°C; total soluble of (48.0%); total solid (88.0%); non – tans (19.0%); tans (28.0%) tans: non – tans (1.5:1); total ash (40.0%). pH (4.5). These results of the tannin

analysis agree appreciably with the values already obtained by other investigators (Oflaherty, F. 1978; Sakar, K. T. 1991).

Physical Observation Of The Leathers

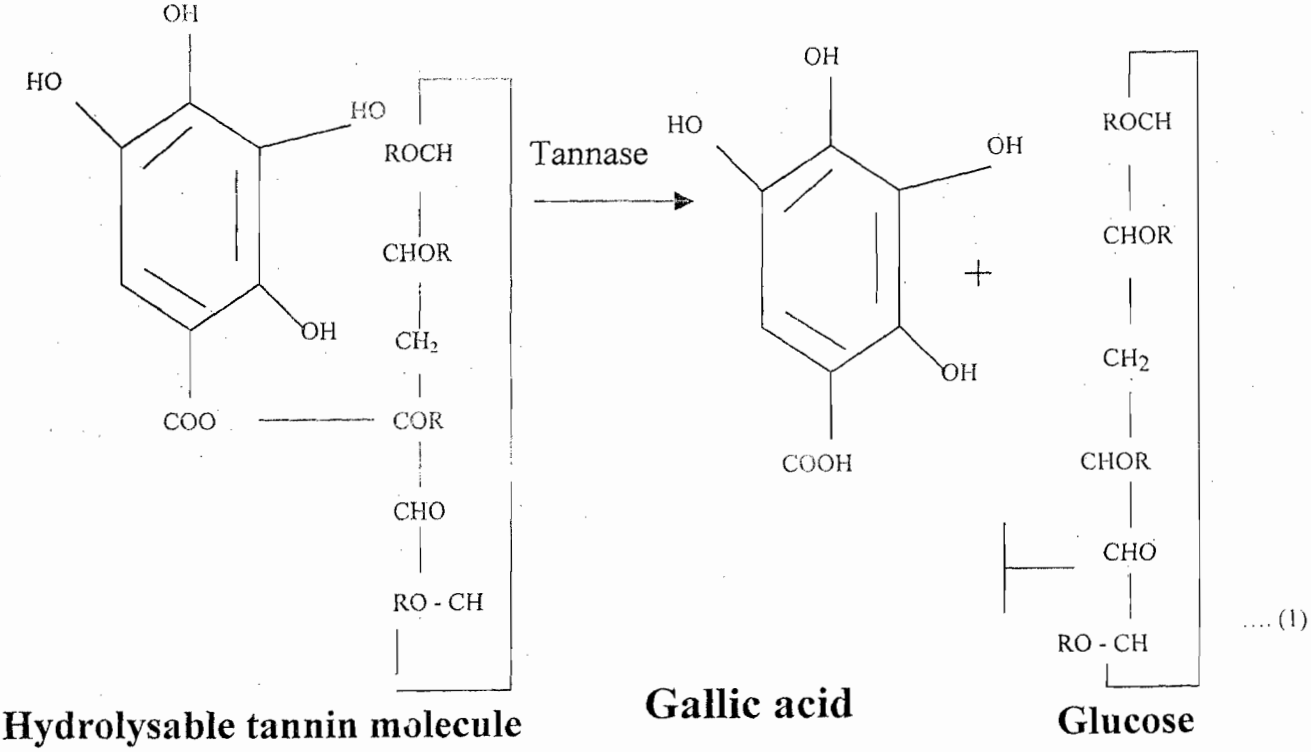
The results indicated that grain appearance were as follows: BS_1 (wrinkled), while those of BS_2 – BS_7 showed gradation of smoothness in the following order: $BS_2 < BS_3 < BS_4 < BS_5 < BS_6 < BS_7$. This trend shows that as the syntan concentration increases the degree of smoothness also increases. Similarly the texture (the degree of softness to touch) increases in the same order. However the substantivity and fullness are in the reversed order $BS_1 > BS_2 > BS_3 > BS_4 > BS_5 > BS_6 > BS_7$. For colour; the progressive changes in the shades of the pale brown colour tc white is as follows; $BS_1 > BS_2 > BS_3 > BS_4 > BS_5 > BS_6 > BS_7$.

From Table 1, the pH values of the liquors before tanning indicated that BS_1 has a higher value than the rest. This is due to the acidic nature of the syntan (i) employed in the blends, (BS_2-BS_7) which tend to increase their hydrogen ion concentrations in solution (Swammy et al, 1984).



(i) **Naphthalene based syntan**

However, there are little or no differences between the pH values of tan–liquors before and after tanning, except that of full Bagaruwa (BS_1) which dropped. This can be attributed to the breakdown or hydrolysis of tannins on standing to acidic organic components such as gallic or ellagic as shown n equation (1).



Hydrolysable tannin molecule **Gallic acid** **Glucose**

Furthermore, the little or no change in pH values of the blend liquors (BS_2 – BS_7) before and after tannage is indicative of the repression activity of the syntan on the Bagaruwa tannin hydrolysis [equation (1)] [Venkataboopathy etal, 1982].

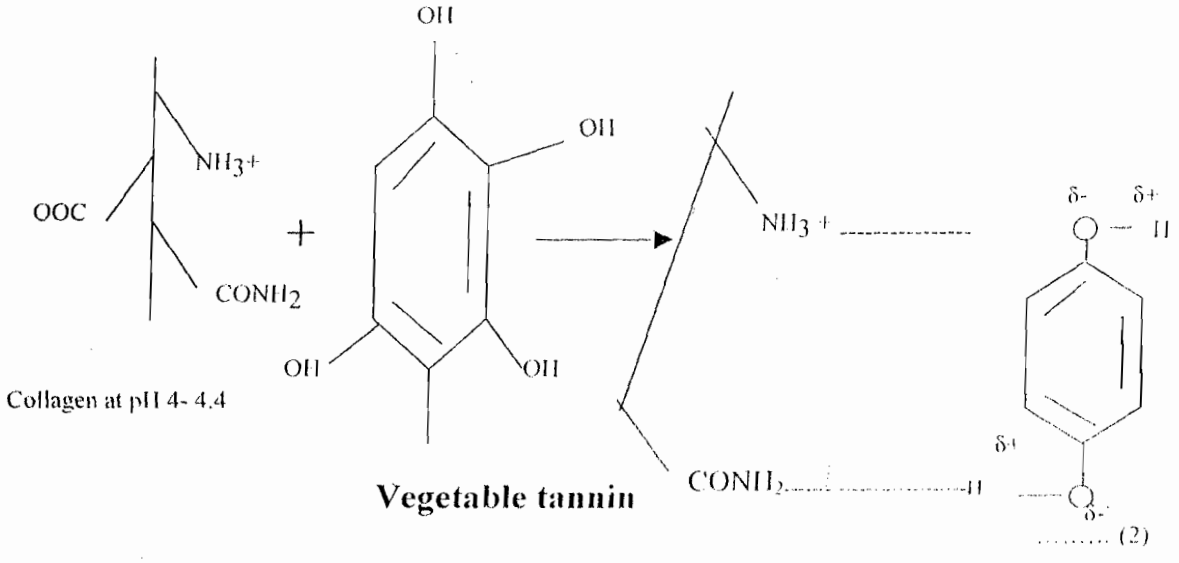
The shrinkage Temperature (Ts) of a leather is a measure of its hydrothermal-stability and therefore degree of bond strength (TNO,1990

IUP/16). This sudden shrinkage is characteristic of a tannage and leather type. For full vegetable tannage (Bagaruwa), the standard value of the shrinkage temperature (by the apparatus employed) is 70°C. From the results in Table 1, the Ts increases steadily from BS_1 to BS_7. This observed trend is indicative of the progressive increase in bond strength between the tannin reactive groups and those of collagen (protein) groups. This suggests that there are increases in the magnitude and number of forces binding the collagen group to the tannins in the blends compared to the full Bagaruwa (BS_1) and syntan (BS_7) (Venkataboopathy et al 1982).

Table 1: pH values of tanning blend liquors and shrinkage temperatures (Ts) of Leathers.

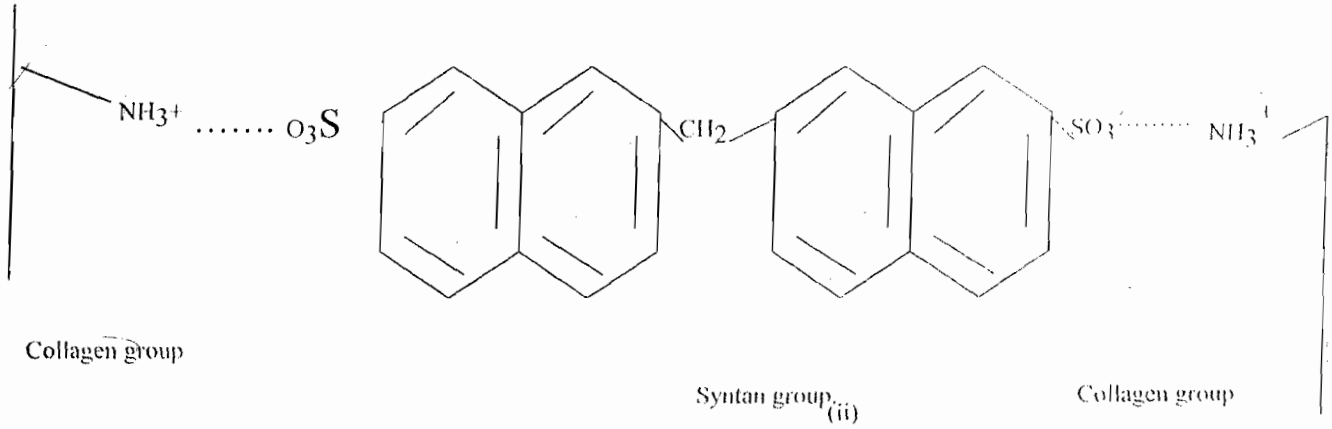
Tanning blend inquor / Leather code	$\%^{W}/_{W}$ Bagaruwa : $\%$ $^{W}/_{W}$ Syntan	pH_b	pH_a	Ts°C	Mould activity
BS_1	60:0	4.4	4.0	73.0	Mould growth
BS_2	50:10	4.2	4.0	74.0	No Mould growth
BS_3	40:20	4.1	4.0	76.0	No Mould growth
BS_4	30:30	4.0	4.1	78.	No Mould growth
BS_5	20:40	3.9	4.0	78	No Mould growth
BS_6	10:50	4.1	4.2	76	No Mould growth
BS_7	0:60	4.0	3.8	68	No Mould growth

Key: pH_b = pH of liquor before tanning; pH_a = pH of liquor after tanning.



..... (2)

Both H – bonding and ionic interactions are exhibited by vegetable tannins as shown in equation (2). With this syntan, the number and magnitude of the cohesive force increases, leading to increases in the values of Ts for blends (see structure below).



(ii)

However, for the Ts values, it is clear as the concentration of the syntan increases, Ts increases to a maximum at BS_4 and BS_5 (78°C)and then decrease to (68°C) at BS_7. This suggests that there are limiting concentrations for which the synergisms of Bagaruwa and syntan are highest (Venkataboopathy et al, 1982).

CONCLUSION

From the preliminary results it can asserted that blending of Bagaruwa tannins with naphthalene-based syntan produces some synergistic effects in terms of the properties of the resultant leathers, than when these tanning materials are used separately. These synergisms are more pronounced for the blends BS_4 (30:30% W/W) and BS_5 (20:40% W/W) in terms of colour, antimould activity, rate of penetration and fixation of tannins and shrinkage temperature.

Thus from these initial results, advantages can be maximised in the utilisation of Bagaruwa since at present in Nigeria, no standard recipe has been developed therefore, blendings become handy as the best alternative to the effective utilisation of Bagaruwa, thus minimising wastages as it is presently being experienced.

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