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## COMPARATIVE STUDIES ON THE EFFECTS OF RAPESEED, COTTONSEED, FISH AND COD-LIVER OIL IN THE PROCESSING OF CHAMOIS LEATHER

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Oil tanning is an essential factor for chamois leather. Oils from three indigenous sources such as fish, cottonseed and rapeseed, were used for the purpose, besides the commonly used cod-liver oil, after their physico-chemical analyses with respect to density and iodine value, acid value, saponification number. Indigenous fish oil gave satisfactory results which were compared with code liver oil tanned products. Shrinkage temperature in both cases was in the reasonable limits of variation (lower, 52-57°; higher 60-65°) under different conditions of processing. The period of tanning, elasticity, softness, velvety feel for fine nap, and water absorption capacity were almost the same under similar conditions. Cotton and rapeseed oil tanned products, although having higher Ts-range of 73-79°, proved inferior to fish oil tanned products.

*Key words:* Chamois leather.

### INTRODUCTION

Chamois leather, a type of soft and velvety leather with fine nap, high elasticity and good water-absorption capacity, is one of the important items of leather industry. It is generally made from goat and sheep skins by the process of oil tanning which is a prerequisite for producing chamoising effects on hide-protein.

*Leather.* Several hypotheses have been put forward to explain the chamoising phenomenon, where unsaturated oils, on polymerization, form a coating around the fibrous hide-protein which is converted into leather by the action of the aldehyde, derived during the auto-oxidation of oils, according to the aborption and acrolin hypothesis [1-4].

The use of cod-liver oil for chamoising is the common practice throughout the world. Efforts were made to examine the effects of indigenous fish oil, in addition to two types of vegetable oils, namely, cottonseed oil and rapeseed oils in the process of chamoising. The physical properties of the products made thereby were compared to the products made by using cod-liver oil to ascertain the suitability of the indigenous oils for chamoising.

### EXPERIMENTAL

(A). *Analysis of oils.* Average density, iodine value, acid value and saponification number of all the four samples of oils (cod-liver oil, fish oil, rapeseed oil and cottonseed oil) were determined according to Official Methods [5]. In the case of iodine value, the Hanus Method was followed. The analytical results are given in Table 1.

(B). *Tanning.* Goat and sheep skins, after unhairing, were put to liming operations for a proper swelling of the protein fibres in the collagen. Deliming was performed with a suitable buffering salt followed by treatment with an enzymatic bating agent to destory the reticulin fibres and blood vessels in the corium.

After degreasing, the water content of the pelt was lowered and the pH was adjusted in such a way that it becomes conducive to a chemical reaction between the basic group of the protein and – CHO group of, aldehydes with the release of hydrogen ion [6,7].

$$R - NH_3 + CH_2O \rightarrow R - NH - CH_2\ OH + H^+$$
$$NH_3 + HCHO \rightarrow NH - CH_2OH + H^+$$

It was then left for a day or two for ageing and treated with the oils. It was hung up in the air to facilitate auto-oxidation and polymerization, forming a film around collagen fibres. The oxidation process was hastened by adding a suitable metallic salt. Oil tannage was effected after pretanning. Oil was also applied directly on pickled pelt. To induce autoxidation heating and drumming are necessary, but overheating may damage the skin fibre, and little heating may cause insufficient tanning, resulting in the production of stiff leather. So the room temperature was maintained between 20-35°.

In the pretanning system formalin in different proportions (2.5, 5, 5.4 and 6% on weight of the pelt) was used

at lower pH and after its fixation, both grain and flesh sides were shaved. It was then treated with 30-40 % oil on shaven weights. Though temperature has a direct bearing on the oxidation process, oiled-pelt was kept hanging in the air for a period of 7, 12 and 30 days. The leather was then washed several times with sodium carbonate and washing soap to remove the excess oil. (If this is treated with aluminium sulphate a slightly water repellent chamois leather will be obtained). After rewashing in fresh water, it was horsed up, dried, staked and buffed and the final product was obtained after its sizing.

## RESULTS AND DISCUSSIONS

*Iodine value.* Earlier investigations for chamoising by oil tanning reveal that marine animal oils of higher iodine value ranging from 140-180 are ideal for the production of chamois leather. The analysis of the local sea fish oil indicates that its iodine value is 146, which is within the normal range and is not far behind that of cod-liver oil. Here, both vegetable oils (rapeseed and cottonseed oil) are unsaturated. But they have lower iodine values.

Iodine value determines the degree of unsaturation which is one of the main factors for proper chamois tanning. Glycerine derived from fish oil during autooxidation which takes place autocatalytically by self-heating, is converted to glyceraldehyde. This actually tans the skins [4]. According to Mathur, there is a direct union of fish oil with hide protein. He contests the role of oxygen in the air for tanning. He thinks that water is necessary and it accumulates at the double bond with the formation of hydroxy acids, which (hydroxyl groups) react with the amino group with the elimination of water [8].

*Fatty acids.* Some workers are of the view that free acids in the oils play an important role. According to Sagoschen and Czepelk 10 to 18 percent free fatty acid in oil is most favourable for chamoising. Wood's experiments have also supported this view [9]. According to Pederson and Galvind, fatty acids do not react with the amino group but with the hydroxyl group and cross links between two collagen molecules are formed [10]. Danby observed an increase in carboxyl groups, with the conclusion that aldehyde carboxy acids act as a tanning agent [11]. Chemical analysis (Table 1) indicates that all oils in question have almost the same acid value which is on the lower side, having little effect on chamoising.

*Unsaponifiables.* None of the materials under review have higher percentage of unsapoinfiable (chain of aliphatic alcohol, pigments and phosphatide). Their range is from 1.1 to 1.9 which is quite negligible.

Its presence in larger proportions is undesirable as it acts partly as an oxidative to accelarator and partly as an inhibitor [12].

*Period and other conditions of tanning.* The period of tanning for chamoising is dependent on various factors, of which the pre-treatment of skin pelt with aldehyde plays an important role. From the examination of Table 2 it will be clear that in the absence of pretanning with aldehyde, oil tanning takes a very long period at room-temperature ranging from 25-35°. Full tanning could not be effected even within 30 days of open air oxidation using untreated raw fish oil or cod oil. The tanning action was negligible with cottonseed oil or rapeseed oil.

Pretanning with aldehyde facilitates oil penetration in the hide protein and shortens the period of tanning. Pretanning with 4 % formalin on pelt weight is an ideal one. The use of 6 % formaldehyde for pretanning makes no marked difference in respect of the period of tanning. It has been observed that full tanning with raw fish oil or codliver oil takes 7-12 days under room temperature. But 30 days of tanning with raw cotton or rapeseed oil gave a fully tanned chamois-type leather but of poor quality. The removal of uncombined oil is quite difficult when compared to fish oil or cod oil.

*Tanning temperature and humidity.* These are also two important factors. If the temperature is high, stiff leather will be produced. In hot summers, oil tanning process is quickened, but the fibres become hard despite high humidity. Room temperature below 40° was found to be suitable for chamoising in humid atmosphere. This supports the view of Kuntzel and Nungesser who have found that polymerizates formed during autoxidation can be better anchored to the fibres of the hydrated skins pelt than the dry ones [12]. Chambered and Michallet have suggested that water has merely the task of bringing the fibres to a swelling condition to permit fish oil penetration [1].

*Properties of the end-product of oil tanning (chamois leather). Shrinkage temperature.* Shrinkage temperature of chamois leather (Table 3) which is always lower than

Table 1. Analytical results.

| S. No. | Materials | Average density | Iodine value | Acid value | Saponification number | Unsaponifiable materils % |
|---|---|---|---|---|---|---|
| 1. | Fish oil | 0.91 | 146 | 1.52 | 194 | 1.9 |
| 2. | Cod-liver oil | 0.923 | 162 | 1.57 | 186 | 1.3 |
| 3. | Cottonseed oil | 0.914 | 117 | 1.2 | 192 | 1.45 |
| 4. | Rapeseed oil | 0.91 | 98 | 1.12 | 173 | 1.1 |

Table 2. Period of oil tanning under different degrees of pretannage.

| S. No. | Material used for oil tanning | Pretanned with formalin pelt % wt.) | Condition of tanning under room temp. (25 – 35°) In 7 days | In 12 days | In 30 days | Remarks |
|---|---|---|---|---|---|---|
| 1. | Fish oil | 0 | Feeble tanning action | Feeble tanning action | Not fully tanned for chamoising | Very slow action, tanning period uncertain |
| | | 2.5 | Partially tanned | Nearly tanned | Tanned | A bit slow chemical action |
| | | 4 | Tanning completed | Already tanned | Already tanned | Quick chemical action with the evolution of pungent smell |
| | | 6 | Fully tanned | Fully tanned | Already tanned | " |
| 2. | Cod liver oil | 0 | Feeble tanning action | Feeble tanning action | Partially tanned | Very slow action tanning period uncertain |
| | | 2.5 | Partially tanned | Nearly tanned | Tanned | A bit slow tanning action |
| | | 4 | Fully tanned | Fully tanned | Already tanned | Immediate penetration and quick chemical action |
| | | 6 | " | " | " | " |
| 3. | Cottonseed oil | 0 | Very feeble tanning action | Very feeble tanning action | Not tanned | Oil stuck on surface and no appreciable change in the pelt |
| | | 2.5 | No appreciable change in the pretanned pelt | Appreciable tanning of the pretanned pelt | Fully tanned | Slow chemical action; long time required for tanning |
| | | 4 | " | Nearly fully tanned | Tanned | Long tanning time but soft cream coloured chamois |
| | | 6 | " | " | " | " |
| 4. | Rapeseed oil | 0 | Very feeble tanning action | Negligible tanning action | Negligible tanning action | Oil stuck on surface; condition of the pelt unchanged |
| | | 2.5 | No appreciable change in pretanned leather | Appreciable tanning of pre-tanned leather | Tanned | Slow chemical action, long time required for tanning |
| | | 4 | Nearly full tanning | Fully tanned | Already tanned | Long time required for tanning soft cream coloured chamois. |
| | | 6 | " | " | " | " |

normal chrome and vegetable tanned leather is not too characteristic.

Generally Ts of oil tanned leather is not higher than collagen. After the removal of extractable fat from oil tanned leather, Ts falls by several degrees. Skins pelt pretanned with 4 % formalin had, Ts of 84° but after oil tanning, it was found to have Ts as low as 57°. This fall in Ts is, according to Belfe, due to the gelatinization of collagen during auto-oxidation as a result of local heating [2]. This may also be due to the adsorption of soap anions to the basic side chains of collagen during washing [13].

*Elasticity and water absorption.* The essential qualities of chamois leather include high elasticity to the extent of 100 % increase on stretching, and good water-absorption capacity ranging from 4 to 5 times of dry weight, in addition to its good nap with soft and velvety feel. Table 4

Table 3. Shrinkage temperature of chamois leather produced under different conditions of pre-tanning.

| S. No. | % of Formalin on pelt wt. for pretanning | Ts of formalin treated pelt before shaving | Shrinkage temperature (Ts) of chamois on treatment with | | | |
|---|---|---|---|---|---|---|
| | | | Fish oil (°C) | Cod oil (°C) | Cottonseed oil (°C) | Rapeseed oil (°C) |
| 1. | 2.5 | 73 -75° | 52 -54° | 56 -57° | 60 -62° | 61 -64° |
| 2. | 4 | 82 -84° | 57 -60° | 60 -65° | 73° | 78 -79° |
| 3. | 6 | 84° | 60° | 65° | 73° | 79° |

took 45-47 sec., showing that these are not suitable for the filtration of petrol or aircraft fuel.

## CONCLUSION

Indigenous fish oil has imparted all essential qualities to the product as is given by cod-liver oil. So the indigenous fish oil is a good substitute for cod oil generally used for the manufacture of chamois leather throughout the world. Cottonseed oil, however, can produce chamois leather of uniform cream colour, coupled with the required softness and elasticity for gloves and garments.

Table 4. Physico-chemical properties attained by chamois leather obtained from pretanned pelt (4 % formalin).

| S. No. | Product from | Ash content (%) | Colour | Elasticity range | Water absorption (drop-test) | Water absorption capacity when fully soaked | Water retention capacity on filtration | Time taken for petrol to pass through | Buffing and softness | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|
| 1. | Fish oil | 1.8 | Yellow | 60-100 % increase | Instantaneous absorption | 4.5 times of dry wt | Good retentivity | 11 sec. | Fine nap with good softness | Well-suited for chamois tanning |
| 2. | Cod oil | 1.8 | Yellow | 65-100 % increase | " | 4.8 times | " | " | " | " |
| 3. | Cottonseed oil | 2.5 | Cream | 25-50 % increase | Delayed by seconds | 4.0 times | Relatively poor | 45 sec. | Coarse fibre, soft feel | Poor elasticity, fine cream colour, suitable for garments |
| 4. | Rapeseed oil | 2.35 | Cream | 25-45 % increase | " | 3.8 times | " | 47 sec. | " | ' |

shows that the properties attained by chamois leather made by using indigenous fish oil and cod-liver oil are almost the same, exhibiting the above mentioned properties. Vegetable oil tanned products have low elasticity and poor water absorption capacity.

*Droptest.* Water drops on the surface of chamois made from fish and cod oils penetrate instantaneously, while the products from vegetable oils offer some negligible resistance to penetration, showing its usefulness as garment and glove leather.

*Ash and colour.* Ash contents of the products in both fish and cod oil are exactly the same. But it was higher in the case of rapeseed and cottonseed oil. The colour imparted to the end product was yellow which is the desired natural colour of chamois leather, while vegetable oils having comparatively higher ash contents produced uniform cream coloured chamois leather, quite suitable for waist coats and gloves.

*Petrol filtration.* Quality chamois leather does not take more than 12 sec. for the filtering of petrol. Cod and fish oil products took 11 sec. indicating its scope of usefulness in filtering gasoline or petrol, while the vegetable oil

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