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LEATHER LUBRICANTS—Pt. VI: STUDIES ON OIL TANNING

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Received on March 29, 1974.

Even though fish oil is the well-known oil tanning agent, other unsaturated oils like rubber seed oil, mustard oil can be used in oil tanning; this indicates that the presence of multiethenoid fatty acid as fatty acid constituent of oil molecule is not a prerequisite for oil tanning.

Oil tanning is one of the oldest modes of converting hides and skins into leather and this is the only tannage wherein the oil incorporated not only tans the skins but also lubricates it. Universally known chamois generally means fish oil-tanned light and loose-textured skins having the grain removed, the name chamois tannage however being derived from primitive tannage of soft skins of goat like antelope *Rupicapra tragus*. Oil tanning was also done with vegetable oil; since two or three centuries rape seed oil-tanned leather called Japanese white leather was produced by Japan[1]; these leathers are not called as chamois. This clearly indicates that the tanning ability of oils is not confined to the oils of marine origin-cod, sardine, herring or whale oil. Though fish oil (e. g. sardine oil) and rape seed oil are semi drying oils, their fatty acid constituents are not similar; fish oils contain mono-, di- and poly-ethenoid unsaturated fatty acids while rape seed oil contains mainly mono- and di-ethenoid unsaturated fatty acids and a very minor amount[2] of triethenoid fatty acids[2] (Table I). This itself indicated that the presence of unsaturated fatty acid constituents having more than two double bonds may not be a prerequisite for tanning potency of a given oil; presence of more than two double bonds in fatty acid chains however might contribute to certain products as a result of oxidative changes of oil incorporated into the skins and hence responsible for better physical characteristics of fish oil-tanned leathers. The mechanism of tanning by marine oils was well studied and well documented.[1-6] The present study is to assess the ability of certain vegetable oils and to assess the role of multi-ethenoid fatty acids of oil molecule in tanning for which purpose oils of seeds of lin, rubber, mustard, tobacco, sunflower and sesame were chosen to tan skins. Skins were also treated with (a) butyl ester of oleic acid and (b) linoleic acid and the ability of these products to tan skins was assessed.

Now-a-days fish oil tannage is mostly carried out as fish oil-formaldehyde combination tannage as the tanning with oil alone requires too much meticulous care in controlling the temperature while stoking and oxidation of fish oil. Hence the possibility of using that vegetable oil/s

TABLE I

IODINE VALUE[x] UNSATURATED FATTY ACIDS OF OILS (PERCENT WEIGHT[3])

Oil	*Iodine value*	*Oleic or other C_{16} monoene acids*	*Linoleic*	*Linolenic or other triethenoid fatty acids*	*C_{18}-C_{20} monoene*	*Erucic*	*Multiethenoid acids C_{20}-C_{24}*	*Total unsaturated fatty acids*
Cod	140-170							
Sardine	170-193	13			24		45	82
Linseed	170-204	13	15	56				84
Rubber seed	140	17	36	24				77
Mustard seed	106-113	31	17	3		42		93
Tobacco seed	145	10	72	1				83
Sunflower seed	125-136	23	54					77
Sesame	103-116	45	41					86

which proved to possess tanning potency in the above experiment was investigaged.

As the purpose of the present study is not to substitute fish oil in making chamois but to make oil-tanned leathers which may find use for clothing or gloving leather and also to know the effect of the nature of unsaturated fatty acid present in oil tanning, skins with grain-on were chosen as the substrate for the study.

Experimental

Delimed pelts (6 nos.) with grain-on were treated with 25% solution of an oil in isopropanol. The application of oil in isopropanol facilitates quicker penetration and uniform distribution of oil within the pelt because it reduces viscosity of the oil to be incorporated and also causes the dehydration of the pelt; its ability to be the common solvent for oil and water is another factor in favour of the penetration of oil.

The skins thus treated were dried in hot chamber at 40°C for a day and again treated with oil in isopropanol. The process of treating and drying overnight was continued till the oil incorporated was 30% of the pelt weight. After completion of this mode of stuffing, the skins were air-dried in hot chamber (40°C) for 10 days; the skins were intermittently staked with hand staking machine for a good opening up of the structure of skins and for good exposure of leather surface to hot air.

The skins are finally degreased with 3.5% of soda ash and 1% of a nonionic wetting agent (Noigen LT 180, Dai-ichi Karkaria-India). For degreasing, the skins were treated first with the solution of half of the specified quantity of detergent in a drum -float-600% of pelt weight, temperature 40-45°C and time 1 hour. The drum was drained, filled with fresh water (600% float) to which half of the specified quantity of soda ash was added, run for 1 hour and drained. This process of washing with soda ash solution was repeated once again using the remaining quantity of soda ash. The skins were then given a final wash using the remaining detergent and then dried; the procedure of final washing is the same as that adopted in the first detergent wash.

The dried skins are staked and buffed first with emery paper of 80 grit and then with 320 grit.

2. Formaldehyde-oil combination tannages

Pickled skins were treated in a drum with 3% of formalin (on pelt weight) for 3 hours after which the skins were depickled by the addition of sodium acetate (3% on pelt weight); as 10% solution was fed to the drum in 4 instalments at an interval of 15 minutes, pH of skins thus depickled was adjusted to 7–8 using sodium bicarbonate (1% on pelt weight). Next day, these leathers were slickered for removing excess water and treated with 30% of oil on pelt weight. The oil, before application, was mixed with 8% of calcium carbonate and treated with ½% of soda ash as 5% solution for making its emulsion; the skins were painted with this emulsion uniformly on both sides and drummed for 6 hours for two consecutive days after which period the skins were air-dried in a hot chamber (40-45°C) for 10 days. These leathers were subsequently degreased and further processed as in experiment 1.

Leathers as such and after rewetting overnight and drying were assessed for their colour and feel. Static water absorption value of these leathers was determined by Kubelkopf method[7]; wherever necessary rate of sinking in water was determined by I. S. I. "Sink Test" method[8]; free oil content of leathers was determined by Official Method[7] and bound oil by I. S. I. methed[9].

Results and discussion

It is seen from Table 2 that all the oils of seeds viz., lin, rubber, mustard, tobacco, sunflower and sesame could tan skins like fish oil. All these leathers could be repeatedly wetted and dried; their leathery nature is not altered as in the case of fish oil-tanned leathers. Among these oil-tanned leathers, sesame oil-tanned leathers were a little empty but on subjecting sesame oil-tanned leathers to tanning with sesame oil once again, the feel of leather was improved. Rubber, mustard, tobacco and sunflower seed oil-tanned leathers were soft and full but not as full as sardine fish oil-tanned leathers; in linseed oil-tanned leather, some amount of resinified oil deposited on the surface at certain places and the leathers were soft at places having less or no deposition. By taking proper care for ensuring complete penetration, the deposition of resinified oil matter on the leather surface could be minimised. This was achieved not only by impregnating the oil as isopropanol solution but also by frequent staking. Rubber, mustard, tobacco, sunflower and sesame oil-tanned leathers are fairly white in colour, while (sardine) fish oil-tanned leathers are cream yellow; skins tanned/treated with ester of oleic or linoleic acid were fairly hard. Water absorbing capacity (Table 3) of linseed and sesame oil-tanned leathers was much less than that of leathers tanned with sardine fish oil and rubber, mustard, tobacco or sunflower seed oils. Sink tests, however, showed that fish oil-tanned leather sank in 1 minute while rubber seed oil-tanned leather required 10-13 minutes for sinking. Shrinkage temperatures of all these leathers were around 60°C. Formaldehyde + rubber seed or tobacco seed oil-tanned leathers are soft and pale yellowish white in colour. They absorb water well (Table 4).

TABLE 2

CHARACTERISTICS OF VARIOUS OIL-TANNED LEATHERS

Oil	*Characteristics of leather*
1. Sardine fish	Full, soft, deep orange coloured leather. Rewetted leather dries soft.
2. Linseed	Full, softer than the fish oil-tanned leather & light if there is no deposition of fixed matter; hard in places having resin deposition; leather is light yellow in colour; rewetted leather dries soft if there is no resin deposition.
3. Rubber seed	Less full than fish oil-tanned leather; soft leather, pale yellow in colour; rewetted leather dries soft.
4. Mustard seed	Pale white leather similar to (3)
5. Tobacco seed	Leather similar to (3)
6. Sunflower seed	Pale white leather similar to (3)
7. Sesame	Pale white soft leather, less full as compared to (3); other properties are similar.
8. Butyl ester of oleic acid	Washed, degreased skin dries into hard material.
9. Butyl ester of linoleic acid	Washed and degreased skin dries into hard material.

TABLE 3

WATER ABSORPTION OF OIL-TANNED LEATHER (KUBELKOPF METHOD)

Oil	% *water absorption*		
	½ hour	*2 hours*	*24 hours*
1. Sardine fish	405	411	427
2. Linseed	210	224	239
3. Rubber seed	408	421	440
4. Mustard seed	373	362	432
5. Tobacco seed	551	587	875
6. Sunflower seed	424	426	451
7. Sesame	277	296	297

TABLE 4

% WATER ABSORPTION OF RUBBER SEED AND TOBACCO SEED OIL-TANNED LEATHER

Leather	*% Water absorption*		
	½ hour	*2 hours*	*24 hours*
Formaldehyde + Fish oil	485	516	640
Formaldehyde + rubber seed oil	426	426	583
Formaldehyde + tobacco seed oil	382	413	498

These results did indicate that the presence of tri-and multi-ethenoid fatty acids i.e., fatty acids having more than three double bonds, is not a prerequisite for oil tanning. Linseed oil, though it tanned the skin, exhibited too much a tendency to resinify and deposit on the surface which is the cause for the decreased water-absorption of linseed oil-tanned leather. This is because linseed oil has more than 50% linoleic acid, a triethenoid fatty acid[2] (Table 1). This fatty acid of linseed oil has too quick a drying tendency and for this reason linseed oil was used in conjunction with fish oil in chamois leather production, particularly, when the oxidative power of the fish oil sample was not upto expectation. The good tanning ability of rubber seed, mustard, tobacco and sunflower seed oils indicates that the presence of a certain minimum amount of di-ethenoid fatty acid (about 17%) (Table 1) is needed, provided the total amount of unsaturated fatty acids is above a certain minimum (about 75%) and the iodine value is 120 and above[2,3]. This is obvious from the percent unsaturated fatty acid composition given in Table 1. The decreased water absorption or emptiness of sesame oil-tanned leathers is perhaps due to the fact that its iodine value is less than 125 and hence its tanning potency is less as compared to other oils studied. The slow sinking of rubber seed oil-tanned leather as compared to fish oil-tanned leather even though percent water absorption values of both the leathers were high, indicated the presence of some oil digradation products in rubber seed oil-tanned leather. This was further substantiated by the free and bound oil-content of these two leathers; fish oil-tanned leather had 1.5% of free oil and 1.5% of bound oil whereas rubber seed oil-tanned leather had 1.7% of free oil and 3.1% of bound oil (the percentages were on hide substance basis); higher bound oil content of rubber seed oil-tanned leather indicates that certain degradation products of the oil are still present in the leather. The fact that butyl esters of oleic or linoleic produce fairly hard leather indicated the possible role of saturated fatty acids present in various oils used in tanning. Only unsaturated fatty acids undergo oxidative changes; saturated fatty acids of glyceride molecule remain in tact. The unsaturated fatty acids undergo oxidative degradation and the degradation products involve themselves in tanning; the intact saturated fatty acid of oil molecule containing the unsaturated fatty acid may contribute to lubrication effect. On this count, esters like butyl esters of linoleic acid may not produce leather as soft as the one produced by unsaturated oil containing such unsaturated fatty acids.

From the foregoing, it is clear that the tanning potency of a given oil is not related to the presence of multi-ethenoid fatty acids in the oil molecule; since the unsaturated fatty acids like oleic acid present in all the oils chosen for study may produce epoxides[4] during auto oxidation of oil and since oils like sunflower oil which contain only oleic and linoleic acids as unsaturated fatty acid constituents can tan skin, it is clear that oil tannage, at least partly, is an epoxide tannage; a semilar view was expressed by others.[4,10]

As the formaldehyde-rubber seed or tobacco seed oil-tanned leathers are soft and supple, they can be used in making gloves and garments; their pale white colour is a point in their favour as compared to orange colour of similarly processed fish oil-tanned leathers. The water absorption properties (Kubelkopf) of formaldehyde fish oil (sardine)-tanned leather and formaldehyde-rubber seed or tobacco seed oil-tanned leather (Table 4) are similar i.e., all these leathers are highly water absorbing in nature. As high water absorbing nature is considered not desirable for garment type of leathers, these skins can be pretanned with chrome and retanned with rubber seed or tobacco seed oil. Preliminary investigations showed that the pretanning of pickled skin with 1% Cr_2O_3 followed by neutralisation with a neutralising syntan and then retanning with rubber seed or tobacco seed oil resulted in soft well-lubricated chrome-oil combination-tanned leather which may be used in making gloves and garments. It is to be noted that chrome-fish oil cambination-tanned leather made, not by this technique, but by the application of chromic acid and fish oil to the skin wherein fish oil while undergoing oxidation also causes reduction of chromic acid into tanning salts, was recommended for gloves and garments."

It is concluded that semi-drying oils like rubber seed or tobacco seed oil which do not have unsaturated fatty acids containing more than two double bonds can be used in oil tanning and tanning potency of oil is not dependent on the presence of tri—or multi-ethenoid fatty acid in the oil molecule. Formaldehyde or mild chrome-tanned leather (1.0% Cr_2O_3) retanned with rubber or tobacco seed oil may be used in making softer type of leathers like gloves and garments.

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