Oils, Fats and Waxes in the Leather Industry*

E. W. NEWBURY
J. GREENEBAUM TANNING CO., CHICAGO, ILL.

Abstract

Leather contains from less than 5% to more than 25% of extractable oil depending upon its type. Oil is usually introduced while the leather is in the wet state but some oils and waxes are used on dry leather for waterproofing and finishing effects. Animal and fish oils are used extensively both in the raw state and treated to make them miscible with water. Oils of vegetable origin have a more limited use.

HIGHLY organized animal skins such as cattle hides consist to a large extent of bundles of fibres composed of collagen. The fibres can be resolved into very small fibrils. During the life of the animal the skin forms a very efficient protective covering, preserved against damage from bacterial action and hydrolysis by other agents by the circulation of the vital fluids in the body. It is the tanners work to continue the preservation of this fibrous structure and to modify it according to the uses to which it may be put.

After freeing the skin of undesirable constituents and the resolution of the fibres to a degree suitable for the particular product desired the collagen is rendered immune to bacterial action and to hydrolysis by tanning it. The tanning action may be accomplished by means of chromium, aluminum or phosphate compounds, or by natural tannins and their synthetic substitutes. Since the dawn of human intelligence it has been done by means of oil. The fixation of collagen can be carried to such a point that the resulting leather under the ordinary conditions of human life is quite permanent.

Fats and related compounds play a very important part in the technology of the tannery other than as a means of tannage. In the following table of partial analyses of various leathers note the percentages of oil present.

	Oak Sole	Chrome Calf	Heavy Upper Retan	Horsehide Garment
Moisture	14.6%	16.3%	15.1%	5.1%
Fat	3.2%	4.6%	20.4%	29.6%
Hide substance (N x 5.62)	29.7%	62.2%	43.6%	52.3%
Tanning material, etc.	52.5%	16.9%	20.9%	13.0%
	100.0	100.0	100.0	100 0

At the conclusion of the tanning process proper the leather is completely saturated with water. It is decidely acid in reaction. The pH value ranges from 3 to 5 but is in some cases raised a point or so by the addition of mild alkaline salts. The primary and most important oiling process is applied to the leather while it is in this condition. By controlling the amounts of oil used and the details of application various effects may be produced. By changes in the kind of oil used still other effects are brought about.

The primary object of the addition of oily substances to leather is to form a film which will to a great extent prevent fibres and fibrils from adhering so tightly together during drying that the leather cannot be subsequently worked out into usable condition. Leather which is dried without oil is quite hard and stiff and entirely worthless for most purposes. It is quite possible to produce a substantially oil free leather by extracting the oil after the leather has been dried and stretched into its final shape, but when this is done the leather must not again be allowed to become saturated with water. Such leather to which a waterproof coating is applied by a japanning process is familiar as patent leather.

Oil serves also as a lubricant by enabling the fibres to move about more easily under strain. This is a very necessary condition in the manufacture of glove and similar leathers where suppleness and extreme flexibility are desirable.

Solid forms of fatty materials are used in very large amounts to impart waterproof qualities and as a means of protection against barnyard and industrial fluids of various kinds containing corrosive chemicals. They are much used in the production of heavy leathers where the amount may reach 25%. Heavy duty army shoes are made from such leather.

The commonest method of application of oils is to add them in the form of an emulsion to wet leather which is being tumbled violently in a vertically revolving wooden drum in a bath of hot water. By regulation of the degree of dispersion of the emulsion and its pH value a given oil may be made to penetrate deeply into the leather or to be precipitated near the surfaces. Emulsions for the purpose are made with soap and free oil, partially oxidized oil, sulfated or phosphated oils or with mixtures of several of them. If conditions are correct the oil is quantitatively removed by the leather, leaving only clear water.

In the cases where it is desirable to incorporate large amounts of solid fats into wet leather a similar procedure is followed except that there is no free water in the drum. The drum is heated and while the leather is tumbling in it the whole of the melted fat is added. An oily material which readily forms emulsions with water is usually present as part of the mixture so that it may more quickly attack the surfaces. Wool grease may be used for this purpose. After a half hour or so of rapid tumbling in the drum the fat mixture is entirely taken up within the voids of the leather, very little remaining upon the surface.

Additional amounts of oil may be applied to the wet leather before drying by sponging it on either as free oil or emulsified. Free oil is frequently brushed on by machine. Such oils are usually of higher viscosity in order that they will remain near or upon the surface for an appreciable time. Oil applied in this way is absorbed in the outer layers during drying as the water is removed. A somewhat less common method, but one which is still in use for some heavy leathers and at one time was used extensively, is to apply oil in the form of a paste with high melting point fats. In this procedure the oil is absorbed from the paste and the solid fats are then removed from the surface and reused. The object of pasting is to allow of the application of varying amounts of oil to portions of the same skin by varying the thickness of the coating applied to different areas.

Dry leather is capable of withstanding considerable heat without damage. This fact makes it possible to saturate the fibrous structure and fill the voids with high melting point waxes and fats to such a degree that the leather is impervious to water and air. The

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*Presented in a symposium on the Industrial Applications of Fats and Fatty Acids held at fall meeting of the American Oil Chemists' Society, Chicago, October 1939.

temperatures necessary to the operation of such a process depend upon the viscosity of the mixture of fats. They may safely approximate 100° C.

Most of the oils used in leather are of animal origin. Among the fatty oils are cod oil, menhaden and other fish body oils, sperm oil (liquid wax), neatsfoot oil and whale oil, the last being known in the trade as train oil. The more prominent of the solid fats are tallow, oleostearine, cod oil stearine, fish oil stearine and wool wax. Cottonseed and corn oils being semi-drying oils are little used for supplying the bulk of the oil in leather but mostly in the form of soaps used as emulsifying agents for other oils. They do, however, have a minor but interesting use in oiling off leathers containing tannin since they tend to prevent darkening by retarding oxidation of the tannin in the surface during drying.

Since most oil is applied to wet leather it is necessary where considerable amounts are to be used that suitable suspensions be easily available and that such suspensions be stable in the presence of small amounts of acid. Much alkali is undesirable especially in the case of chrome leather. Sulfated oils make the use of soap unnecessary for many leathers. They may be used alone or in admixture with untreated oils. Sulfated cod and neatsfoot oils are used in large amounts. Depending upon the degree of sulfation and neutralization some of them are very nearly water soluble. They contain notable amounts of oxidized fatty acids soluble in alcohol but not in petroleum ether and usually considerable free fatty acids. Two typical analyses, obtained by the Official Method of the A.L.C.A., are given below.

	Sulfated Neatsfoot	Sulfated Cod
Water	24.74%	25.26%
Unsaponifiable	0.46%	0.35%
Ammonia (NH_3)	0.13%	0.00%
Sodium as soap	0.15%	0.35%
Neutralized combined SO_3	4.44%	3.86%
Total salts and impurities	1.39%	1.01%
Combined and free fatty acids	26.95%	21.38%
Neutral fat, by difference	41.74%	47.79%
	100.00	100.00
Total ash	4.50%	4.26%
Free fatty acids as oleic	22.98%	17.94%
Oxidized fatty acids	10.63%	4.60%
Unoxidized fatty acids		
Melting point	38.0°C	27.5°C
Iodine value	58.3	95.0
pH value, 10% emulsion	6.14	6.54

Another type of oil which is usually purchased as an emulsion with water is partially oxidized cod or oil of similar character. It usually requires some additional emulsification with sulfated oil or soap. It may be used alone or with admixture of other oils. The large percentage of oxidized fatty acids in this product is responsible for its ability to be absorbed by wet leather and its stability in emulsions. Oils of this type are known as Moellons, an analysis of a common variety follows.

Water	19.70%
Ash	0.01%
Unsaponifiable	0.16%
Unoxidized fatty acids	
Melting point	31.5°C
Iodine value	63.3
Free fatty acids as oleic	13.04%

In order to modify the properties of technical emulsions it is sometimes advantageous to add egg yolk, a commercial preserved product consisting in reality of the whole de-shelled egg. The lecithins present and the albumin are responsible for its beneficial effect in equalizing the distribution of fat in the leather. Lecithins from soy beans have been of interest in the past few years as a constituent of fat liquoring mixtures but they do not as yet appear to have come into great use for this purpose.

There are a considerable number of proprietary treated oils on the market for tannery use. They are various combinations of sulfated, phosphated, oxidized and raw oils and some of them contain wetting agents such as the sulfonated higher alcohols. A few have appeared which have a few percent of insoluble suspended matter; one in particular which has come to our attention contains about 2% of free silica. Some are diluted with mineral oil for use where mineral oil is desirable. Analysis becomes a very complicated procedure and the determination of the actual varieties of oil or oils present frequently becomes impossible.

In the process of drying leather after tannage and oiling there is considerable change in the characteristics of the oil. The absorption of oxygen is quite rapid and in some cases the reactions taking place are so strongly exothermic as to cause the temperature to reach the kindling point. To avoid such difficulty it is necessary to modify the oil mixture either by adding mineral oil or by a change in the varieties of fatty oils. Small amounts of iron salts appear to be active catalysts and it is quite possible that other substances behave similarly. In a finished leather there are present moisture, iron and aluminum complexes, free tannin, and chromium salts if the leather has been tanned with chromium compounds. There may be present also sugar, sodium chloride and sulfate, magnesium sulfate, barium sulfate and titanium oxide. More rarely we encounted free sulfurous acid, free sulfur, formate and acetate ions and lactic acid. Most leathers contain easily ionized sulfate ion so that aqueous extracts contain traces of sulfuric acid and have pH values well below 7. Some of the materials in leather appear to act as inhibitors toward oxidation.

Due to these changes it is quite likely that there is often an auxiliary tannage by oil which influences the properties of the leather. There is some evidence that such an action takes place when cod oils are used in large amount or other oils which contain fatty acid radicals having four double bonds. The familiar chamois leather is produced by such an oil tannage and in this case the oil is the only tanning agent present. In the chamoising process cod oil or its equivalent is beaten into wet skins, neutral or slightly acid, for several periods alternating with rest periods with the stock in piles. The skins gradually assume a yellow color and after pressing and washing with dilute alkali to remove most of the excess oil are found to have fixed up to 7% of oil which cannot be extracted. During the tanning process considerable acrylic aldehyde is produced and water is lost. Heat is liberated in such large amounts that it is necessary to spread out the stock at intervals to prevent damage.

At the present time there appears to be an increasing interest in the use of modified mineral oils. Some of these are fair emulsifying agents and can be used to replace some of the fatty oils. While this interest is largely experimental in character it may be expected that further research will cause a considerable lessening of the demand for fats. Very large amounts of mineral waxes and petrolatums are used successfully at the present time in place of hard fats particularly for the impregnation of heavy leathers. Most of the heavy petroleum oils as used in leather appear to suffer no alteration over ordinary periods of time and hence have some advantage over fatty oils for this reason.

Waxes such as carnauba are very little used in leather but are used in important amounts as ingredients of leather finishes to which they contribute gloss and a certain amount of proofing against water damage.

Abstracts

Oils and Fats

Edited by
M. M. PISKUR

CHROMATOGRAPHIC SEPARATION OF A MIXTURE OF PALMITIC, STEARIC AND OLEIC ACIDS. Carmela Manunta. *Helv. Chim. Acta, 22,* 1156-60 (1939). A mixt. of equal parts of the 3 acids was dissolved in petr. ether and percolated thru a chromatographic column of dried $MgSO_4 1/2H_2O$. A nearly complete sepn. was obtained. The palmitic acid remained in the upper part of the column and the stearic acid in the lower part of the relatively barren zone between. The oleic acid was not adsorbed. Similar results were obtained with a column of franconite. (*Chem. Abs.*)

EMULSIFYING AGENTS FOR MARGIN. O. K. Palladina. *Masloboino Zhirovoe Delo 1939,* No. 2, 30-2. — Directions are given for polymerizing glycerol, preferably to triglycerol (mol. wt. 270). Exhaustive esterification of the polyglycerol with a suitable fatty acid, using 0.2% MgO or 1% anhydrous Na_3PO_4 as catalyst, is the next step in making an active emulsifier. A phosphatide group, esterified once with hydroxyethyltrimethylammonium hydroxide, provides a potent hydrophilic group. A good emulsifier for margarin should be miscible with water and should be effective at 0.5% concn. in fat-water mixts. (*Chem. Abs.*)

MODIFICATION OF FAT IN FROZEN PORK MEAT AFTER PROLONGED STORAGE. Ie. I. Novikova. *Kholodil 'naya Prom. 16,* No. 4, 30-5 (1938); — If the meat is kept at — 18°, there is no change in the fat over a period of 1 yr. If stored at — 8°, the fat undergoes chem. and organoleptic changes. The surface layer yellows (even in 6 months) and acquires a stearic taste; in 1 yr. the phenomenon has penetrated to a depth of 0.25-0.40 cm. Frozen pork meat should therefore not be stored at -8° for more than 3-4 months. (*Chem. Abs.*)

THE EFFECT OF COD LIVER OIL AND FISH MEAL ON THE FLAVOR OF POULTRY PRODUCTS. E. M. Cruickshank. *Proc. 7th World's Poultry Congr., Cleveland 1939,* 539-42. — Prolonged feeding of rations contg. fish oils causes an increase in the degree of unsatn. of both body fat and yolk fat.

ADULTERATION OF CHAD BUTTER, ITS DETECTION, VALUE OF THE VALENTA NUMBER. P. Creach. *Ann. fals. 32,* 4-16 (1939). — The various forms of adulteration likely to be encountered in this butter, made in Chad, are discussed. The most frequent ones are the addn. of arachis, sesame and Balanites aegyptica. Sesame oil is readily detected in amts. of 2.5% (and even as little as 1-1.5%) by the Villavecchia and Fabrics color test. The Valenta test (crit. soln. temp. in glacial AcOH) is suitable for detection in the field of the above oils, as well as of castor oil and beef and mutton fats, which also may occasionally be encountered as adulterants (*Chem. Abs.*)

POSSIBLE DELETERIOUS EFFECTS OF USING SOAP SUBSTITUTES IN DENTIFRICES. Sidney Epstein, A. H. Throndson, Wm. Dock and M. L. Tainter. *J. Am. Dental Assoc. 26,* 1461-71 (1939). — Na lauryl sulfate and Na lauryl sulfoacetate, which are used as detergents in certain dentifrices, were irritating to the nose. They produced extensive conjunctivitis in rabbits, similar to, but more intense than, that produced by soap U. S. P. (*Chem. Abs.*)

RICINUS COMMUNIS. I. OXIDATION OF RICINOLEIC ACID. St. Elmo Brady. *J. Am. Chem. Soc. 61,* 3464-7 (1939). Summary: The oxidation of ethyl ricinoleate in dry acetone yields the liquid acids, caproic, heptylic and caprylic; and the solid acids, β-hydroxypelargonic acid, azelaic, suberic, and an acid of m.p. 96°. The oxidation of ricinoleic acid in alkaline permanganate solution at 0° gave two trihydroxstearic acids already known, m.p. 110° and 141°, respectively, in approximately equal amounts. The oxidation of ricinelaidic acid, on the other hand, gave a large percentage of the acid, m.p. 110°, and a small amount of the acid, m.p. 141°. The oxidation of both the trihydroxystearic acids obtained from ricinoleic and ricinelaidic acids, resp., with periodic acid, resulted in the same products. β-hydroxypelargonic aldehyde and aldehydoazelaic acid.

A METHOD FOR THE PREPARATION OF α, β-DIGLYCERIDES OF FATTY ACIDS. B. F. Daubert and C. G. King. *J. Am. Chem. Soc. 61,* 3328-30 (1939). A new method for synthesis of α, β or 1,2-diglycerides has been described, in which sodium glyceroxide and benzyl chloroformate served as intermediates. Good yields were obtained and the reaction conditions made it possible to avoid the common β — to α — shift in structure. 1,2-dipalmitin, m.p. 64°, 1,2-dimyristin, m.p. 59° and 1,2-dibenzoate of glycerol, m.p. 59°, were prepared and their structures were verified by making derivatives of known constitution. A solution of 1,2-dipalmitin in 0.1 to 0.25 N alcoholic hydrochloric acid and ammonia underwent a rapid change in structure, but the analogous 1,2-dibenzoate was stable under the same conditions of exposure.

THE DISTRIBUTION OF THE FATTY ACIDS IN HALIBUT INTESTINAL OIL, WITH A NOTE ON THE PRESENCE OF FREE FATTY ACIDS IN THE INTESTINES OF FISH. John Arnold Lovern and Richard Alan Morton. *Biochem. J. 33,* 1734-9 (1939). A large quantity of halibut intestines was extracted with ether and the resulting oil was partially separated into its components, the processes used being alkali-washing, acetone precipitation and crystallization and molecular distillation. The products separated for examination included free fatty acids, phosphatides, vitamin and cholesterol esters and a "neutralized" oil. The fatty acids recovered from these products were quantitatively analysed and it is shown that both vitamin A and cholesterol were esterified with all the various fatty acids present, the amounts of the different esters being proportional to