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TREATING OF LEATHER

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This invention relates to the treating of leather, more particularly to compositions which may be used to replace neat's-foot oil and other oils in various leather treating processes.

The mere conversion of raw skin into leather does not as a rule make it suitable for the purposes for which the leather is to be used. Usually the leather receives quite extensive treatments following the actual tanning. In many cases, the next step after the tanning process is the incorporation of oils or fats into the leather in order to lubricate the fibers so as to make the leather more soft and pliable and to increase its tensile strength and resistance to tearing. Often times this is carried out by a process known as fat-liquoring, in which the oil is usually applied to the leather in the form of an aqueous emulsion. In most cases these fat-liquor emulsions consist principally of an oil, such as neat's-foot oil or cod oil, with an emulsifier, such as a sulfonated oil or a soap, and water.

In selecting oils to be used in these fat-liquoring emulsions it is advisable to choose an oil which has a low cloud and pour point, and whose fatty acid constituents are principally fatty acids having low solidification points. If oils are used which have medium to high cloud and pour points, the leather will frequently become coated with a film or spew of solidified fat when it is subjected to temperatures below room temperature. Also, since the oils, after they have been incorporated into the leather, may undergo gradual hydrolysis with liberation of free fatty acids, it is important that at least the majority of the constituent fatty acids of the oil have relatively low solidification points; otherwise the leather, even though it has been treated with an oil which is liquid at ordinary temperatures, may in time become coated with a film or spew of solidified free fatty acids. Since a spew of either the solidified fat or the solidified free fatty acids detracts from the appearance of the leather, it is highly undesirable. Low cold test neat's-foot oil is admirably suited to the treating of leather as it is not only very fluid itself, but also its liberated free fatty acids are for the most part liquid at ordinary temperatures met with in practice. In addition to its fluidity and low solidification point, such neat's-foot oil has other desirable characteristics such as light color, satisfactory odor, good properties of lubrication, etc., which make it a highly desirable material to use in other steps of leather treating as well as for fat-liquoring leather. Various materials have been proposed as substitutes for neat's-foot oil,

but none of them, however, has been able to satisfactorily replace it to any great extent. In many cases the pliability, strength, plumpness and other qualities of leather fat-liquored with such materials which have been proposed as substitutes for neat's-foot oil, have not been entirely satisfactory. In fact, even neat's-foot oil itself does not give entirely satisfactory results in some cases; and in view of the fact that it is relatively high priced, there has been a constant demand for a product that would not only replace neat's-foot oil as far as performance is concerned, but also as a matter of economic importance, a material which would be less expensive.

It is the object of this invention to replace neat's-foot oil with low cost compositions of material in various leather treating processes.

It is also the object of this invention to provide novel and improved compositions to be used as constituents of fat-liquoring baths, which will impart highly desirable properties of plumpness, filling, lubrication, etc. to leather treated therewith.

Another object of the invention is to provide a process for imparting improved plumpness, filling, and lubrication to leather fibers.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

It has now been found that the foregoing and other objects of the invention may be accomplished by incorporating in or applying to leather, a composition comprising a blown fatty oil and an alkyl ester of a fatty residue. The oily composition may be employed as such, or it may be dispersed or emulsified in an aqueous medium. An emulsifying agent may be blended with the composition, or an alkaline agent may be added to saponify a portion thereof, thus forming a soap which functions as the emulsifier.

Blown oils have high viscosity, good body, large molecular weight, are high in oxy fat content, and give plumpness and good filling to leather. They do not penetrate leather as easily as many oils do, but instead tend to stay on the surface and give a characteristic surface feel. Furthermore, they help in the compounding of homogeneous mixtures when they are used in fat-liquoring baths and for other purposes in admixture with other materials. The expression "blown oil" as used in the specification and claims connotes any animal or vegetable oil, fat or wax which has been partially oxidized or polymerized, or has had its viscosity increased by blowing air through it.

The esters used in accordance with the inven-

tion are low in viscosity, are very fluid and have a relatively low cold test. They readily penetrate into the fibers and give better lubrication than is obtained with the oils usually used in fat-liquoring baths. These esters can be easily spread on the surface, giving a thin film. Also in most cases they are of a light color and are free from objectionable odors. Esters may be selected which have physical properties more or less opposite to the physical properties of the blown oils, and thus the ester and the oil will bolster each other to give a complete well-rounded oil compound for the treating of leather. Thus by using a proper mixture of ingredients each having desirable complementary properties to the other, results are obtained that are definitely superior to those obtained by the use of individual ingredients alone.

The blown oils may be prepared in accordance with any known and suitable process including that disclosed and claimed in U. S. application Serial No. 334,652, filed on May 11, 1940. Likewise any suitable non-drying or semi-drying oil may be subjected to oxidation and/or polymerization and used in the composition of the invention. Suitable oils may comprise, inter alia, soybean oil, olive oil, rapeseed oil, rice bran oil, teaseed oil, peanut oil, corn oil, neat's-foot oil, sperm oil, cottonseed oil, castor oil, lard oil, etc. or any suitable mixture of these and/or other fatty oils or waxes.

The esters which may be used in the invention comprise suitable esters produced by esterifying monohydric alcohols with monobasic aliphatic acids and suitable mono and diesters produced by esterifying dihydric alcohols with monobasic aliphatic acids. Examples of such esters include monohydric alcoholic esters of the higher fatty or similar acids such as aliphatic or cyclo aliphatic types derived from petroleum by oxidation, cracking, etc. One such type is the naphthenic acids which are so similar to the higher fatty acids, as far as this invention is concerned, that they will hereinafter be included within the generic term "higher fatty acids." Esters produced by esterifying acids such as stearic, oleic, palmitic, lauric, caprylic, capric, ricinoleic, linoleic, naphthenic, etc. acids with alcohols such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, isoamyl, etc. alcohols are illustrative of such monohydric alcoholic esters. While the foregoing type of esters is preferred, the esters produced by the esterification of fatty alcohols, containing 8 or more carbon atoms, with the lower fatty acids, are also well adapted for use in the invention. As examples of the latter type the following are illustrative: octyl formate, decyl acetate, lauryl acetate, myristyl propionate, palmityl acetate, oleyl butyrate, stearyl acetate, naphthenyl propionate, ricinoleyl formate, etc. Other esters which have been found to be useful include the mono and diesters of dihydric alcohols, such as, for example, the monoethylene and diethylene glycol mono and diesters of lauric, palmitic, oleic, etc. acids. It is to be understood, of course, that the esters which have been listed are only illustrative of the esters which may be used, and by no means are such examples to be construed in a limiting sense.

It is preferred to use esters, which either alone or when admixed with the blown oils, will have a cloud point below at least 42° F. and a pour point below at least 38° F. and in a number of cases, especially when dark leather is to be treated, the ester or the blown oil and ester com-

position should preferably have a cloud point below 22° F. and a pour point below 18° F. However, in some cases, such as for stuffing sole leather, esters may be used having solidification points even above 42° F. The expression "cloud point" is used in the specification and claims to connote the temperature at which the compositions of the invention become cloudy on being chilled; and the expressions "pour point" and "cold test" are used synonymously to connote the lowest temperature at which the compositions of the invention will flow.

The relative proportions of the two components of the composition of the invention may be varied within wide limits, it being preferred, however, that the synthetic esters comprise at least 35% and up to 95% of the composition. When greater lubrication with less filling, plumpness, etc. is desired, a larger proportion of the esters than of the blown oil should be used; and conversely when less lubrication and more filling, plumpness, etc. is desired, a smaller proportion of ester and a larger proportion of blown oil should be used. By suitably varying the ratios of the two components almost any desired result may be obtained. Other substances may also be included in the composition, such as, for example, animal, vegetable and mineral oils and waxes, derivatives thereof, such as the amides, amines, ketones, ethers, etc., as well as products produced therefrom by sulfonation, sulfation, phosphation, etc. Other fatty esters may also be included such as the mono or diglycerides of the higher fatty acids and sulfonation or sulfation products thereof.

By far the most extensive use of neat's-foot oil in treating leather is in fat-liquoring processes. By this invention neat's-foot oil may be entirely replaced in such processes with compositions comprising an ester and a blown oil. The compositions of the invention have very desirable properties of fluidity, light color, very little odor, and good lubrication, spreading, and penetrating power, etc., which make them very applicable for replacing neat's-foot oil. In many cases certain of the compositions, in addition to being less expensive than neat's-foot oil, give much more satisfactory results than the best neat's-foot oil obtainable.

In using the compositions of the invention in the fat-liquoring of leather, they may be applied to leather in any usual or suitable manner. They may be applied as such or in aqueous emulsions. An emulsifier may be blended with the compositions to render them dispersible; or common alkaline agents, such as alkalis, carbonates, borax, triethanolamine, etc. may be added to render the compositions dispersible in an aqueous medium. The application of the compositions to the leather may be accomplished by any usual or suitable process, such as, for example, by tumbling the hides in a rotating drum containing the emulsified compositions. In some cases it may be desirable to apply a concentrated emulsion of the compositions or the compositions as such to the leather by hand. Such a method is particularly applicable to the fat-liquoring of furs by swabbing the compositions onto the flesh side of the fur, or the compositions may be mixed with some substance such as egg yolk to form a thick paste which is swabbed onto the flesh side of the fur.

Not only may these compositions be used in fat-liquoring of leather, but they may also be used in other steps of the treating of leather. For example, it has been found that excellent

compositions for the finishing of certain types of leather, e. g. sole leather, may be prepared by admixing various waxes, gums, and mucilaginous materials with the blown oil-synthetic ester compositions of the invention. Many such finishing compositions are prepared using vegetable oils with such waxes, gums, and mucilaginous material; however, the ester-blown oil compositions are of particular value in replacing the oils in such finishing compounds.

Also the compositions of the invention are well adapted to the oiling-off of leather in the later stages of the finishing operations in place of using neat's-foot oil. For this purpose the compositions may be used as is or in aqueous emulsions. The oiling-off may be done either by hand or by machines adapted for that purpose. As the compositions spread very easily and the ester component penetrates readily to give good lubrication while the blown component gives a desirable characteristic surface feel to the leather, they are particularly suitable for replacing neat's-foot oil for this purpose. The compositions may be used in such operations either alone or in combination with other materials, e. g. sulfated soybean oil, sulfated rice bean oil, etc.

It will be obvious to one skilled in the art that the ester-blown oil compositions hereinabove mentioned may replace neat's-foot oil and various other oils in leather treating steps other than in the specific ones already discussed. By way of illustration, there may be mentioned the rejuvenation of brittle, soiled leathers by first scrubbing the leather with a soap solution, then smearing a thin film of one of the ester-blown oil compositions of the invention over the grain surface of the leather while it is still thoroughly wet and allowing the leather to dry slowly.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following examples which are given merely to further illustrate the invention and are not to be construed in a limiting sense, all parts given being by weight.

Example I

An excellent replacement for neat's-foot oil to be used in fat-liquoring leather and in other leather treating processes may be prepared by mixing together 40 parts of blown soybean oil and 60 parts of butyl oleate. Such a mixture was found to have a cloud point of 10° F. and a pour point of 2° F.

Example II

A composition containing 50 parts of methyl oleate and 50 parts of blown soybean oil had a pour point of 20° F.; it did not show any cloud point whatsoever. Such a composition when used for the treating of leather, in fat-liquoring baths or otherwise, imparts to the leather highly desirable properties of good lubrication, filling, etc. and a desirable surface feel.

Example III

In the fat-liquoring of light leathers as, for example, glove leather, upper leather, calfskins, etc., a composition containing 70 parts of isobutyl ricinoleate and 30 parts of blown peanut oil is very satisfactory. Such a composition had a cloud point of 15° F. and a pour point of 13° F.

Example IV

In a case where it may be desired to have an oily material having cloud and pour points some-

what higher than the cloud and pour points of the compositions given in Examples I, II, and III, a composition containing 70 parts of butyl palmitate and 30 parts of blown sperm oil may be used, as such a mixture had a cloud point of 46° F. and pour point of 42° F. This could be used for fat-liquoring or oiling off white leather as on such leather any spew that might tend to form on the surface of the leather from the oily material would for all practical purposes be relatively unnoticeable in most cases. Also such compositions could well be used as constituents of finishing compounds for sole leather to replace various animal, vegetable or mineral oils which are used therein.

Example V

A finishing compound for sole leather to be used for sponging and washing sole leather in the finishing operations may be made up as follows:

	Parts
Wool grease.....	5.0
Rosin.....	7.0
Paraffin wax.....	2.0
Carnauba wax.....	1.0
Dry sodium hydroxide.....	3.5
Gelatin.....	5.0
Water.....	66.5
Any of the compositions of Examples I, II, III, or IV.....	10.0
	100.0

Example VI

For oiling off side leather before tacking, use the following mix:

	Parts
Sulfated soybean oil.....	3
Any of the compositions of Examples I, II, or III.....	2

In some cases as with white leather, 2 parts of the composition of Example IV may also be used. In using such a mixture, make up a 50% emulsion thereof in warm water, and apply by swabbing on the grain side of the leather before tacking up on the boards, or in case the leather is pasted out on panel boards for drying, apply the oiling-off mix immediately after pasting out.

From the above description and examples, it can readily be seen that compositions comprising a blown oil and an alkyl ester of a fatty residue have properties which make them particularly applicable for leather treating processes and especially in replacing neat's-foot oil in such processes. Neat's-foot oil which has a low cold test is very much in demand. Many of the ester-blown oil compositions in addition to having other properties superior to those of neat's-foot oil also have lower cloud and pour points than does the best grade of neat's-foot oil. The composition of Example I, which is one of the preferred compositions of the invention, has cloud and pour points which are lower than the cloud and pour points of almost any neat's-foot oil obtainable. In Example I the cloud and pour points of the composition are given as 10° F. and 2° F. respectively. However, by varying the ratio of blown oil and ester, it has been possible to produce mixtures of the two components of Example I, having a cloud point as low as 5° F. and a pour point of 0° F. or lower.

In addition to all of their other desirable properties, the compositions of the invention are in many cases less expensive than neat's-foot oil and other oils used in leather treating.

In some cases it has been found that the ester

component may be used to advantage without admixing with a blown oil. For example, in the oiling-off of leather it may be desirable to use a mixture such as given in Example VI, except that the blown oil is entirely replaced with one of the esters. Also in some cases of fat-liquoring and finishing of certain leathers, it has been found to be desirable to use the esters alone instead of in conjunction with the blown oils, and it is intended that such uses of the esters be included within the scope of this invention. For example, if excellent lubrication of the leather fiber with consequent softness and pliability is desired without the leather having the plumpness and characteristic surface feel given to it by the blown oils, it may be desirable to use the esters alone. When the esters are so used, they may be applied to the leather just as the ester-blown oil compositions are applied and in any of the processes where the ester-blown oil compositions may be used. The expression "leather" is used herein to connote the class of hides, skins, furs and pelts.

Since certain changes in carrying out the above process and certain modifications in the composition which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all the generic and specific features of the invention herein described and all statements of the scope of the invention, which, as a matter of language, might be said to fall therebetween; and that they are intended to be inclusive in scope and not exclusive, in that if desired, other materials may be added to our novel composition of matter herein claimed without departing from the spirit of the invention. Particularly it is to be understood that in said claims, ingredients or components recited in the singular are intended to include compatible mixtures of said ingredients wherever the sense permits.

Having described our invention, what we claim as new and desire to secure by Letters Patents, is:

1. In a process of treating natural leather, the step which comprises applying thereto a composition the active components of which consist essentially of a blown fatty oil and a water-insoluble liquid ester containing at least 9 carbon atoms and selected from the class consisting of esters or monohydric alcohols with higher fatty acids, esters of fatty alcohols, containing at least 8 carbon atoms, with lower fatty acids, monoesters of dihydric alcohols with higher fatty acids, and diesters of dihydric alcohols with higher fatty acids.

2. In a process of fat-liquoring leather, the step which comprises incorporating into leather a composition the active components of which consist essentially of a blown fatty oil and a water-insoluble liquid ester containing at least 9 carbon atoms and selected from the class consisting of esters of monohydric alcohols with higher fatty acids, esters of fatty alcohols, containing at least 8 carbon atoms, with lower fatty acids, monoesters of dihydric alcohols with higher fatty acids, and diesters of dihydric alcohols with higher fatty acids.

3. In a process of oiling-off leather, the step which comprises applying thereto a composition the active components of which consist essentially of a blown fatty oil and a water-insoluble

liquid ester containing at least 9 carbon atoms and selected from the class consisting of esters of monohydric alcohols with higher fatty acids, esters of fatty alcohols, containing at least 8 carbon atoms, with lower fatty acids, monoesters of dihydric alcohols with higher fatty acids, and diesters of dihydric alcohols with higher fatty acids.

4. In a process of finishing natural leather, the step which comprises applying thereto a composition the active components of which consist essentially of a blown fatty oil and a water-insoluble liquid ester containing at least 9 carbon atoms and selected from the class consisting of esters of monohydric alcohols with higher fatty acids, esters of fatty alcohols, containing at least 8 carbon atoms, with lower fatty acids, monoesters of dihydric alcohols with higher fatty acids, and diesters of dihydric alcohols with higher fatty acids.

5. In a process of treating natural leather, the step which comprises applying thereto a composition the active components of which consist essentially of a blown fatty oil and a water-insoluble liquid monohydric alcohol ester of a higher fatty acid, said ester containing at least 9 carbon atoms.

6. In a process of fat-liquoring leather, the step which comprises applying to leather an emulsified composition the active components of which consist essentially of a blown fatty oil and a water-insoluble liquid monohydric alcohol ester of a higher fatty acid, said ester containing at least 9 carbon atoms.

7. A process of treating natural leather, which comprises incorporating into leather a composition the active components of which consist essentially of blown soybean oil and a water-insoluble liquid monohydric alcohol ester of a higher fatty acid, said ester containing at least 9 carbon atoms.

8. A process of treating natural leather, which comprises incorporating into leather a composition the active components of which consist essentially of a blown vegetable oil and butyl oleate.

9. A method of fat-liquoring leather which comprises incorporating into the leather a composition, the active components of which consist essentially of a blown fatty oil and a water-insoluble liquid monohydric alcohol ester of a fatty acid, said ester containing at least 9 carbon atoms.

10. A method of fat-liquoring leather which comprises incorporating into the leather a composition, the active components of which consist essentially of a blown fatty oil and a water-insoluble liquid monohydric alcohol ester of a higher fatty acid, said ester containing at least 9 carbon atoms.

11. A method of treating natural leather which comprises applying thereto a composition, the active components of which consist essentially of blown soybean oil and butyl oleate.

12. A method of treating natural leather which comprises applying thereto a composition, the active components of which consist essentially of blown sperm oil and methyl oleate.

13. A method of treating natural leather which comprises applying thereto a composition, the active components of which consist essentially of blown teaseed oil and a water-insoluble monohydric alcohol ester of a fatty acid, said ester containing at least 9 carbon atoms.

14. A method of treating natural leather which comprises applying thereto a composition, the active components of which consist essentially of a blown vegetable oil and methyl oleate.

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