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LUBRICANTS FOR HIDES AND LEATHER

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No Drawing. Continuation-in-part of application Ser. No. 880,432, Nov. 26, 1969, which is a continuation-in-part of application Ser. No. 482,639, Aug. 25, 1965, both now abandoned. This application June 21, 1971, Ser. No. 155,339

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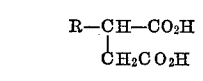
ABSTRACT OF THE DISCLOSURE

A lubricating agent for hides and leathers in the form of an emulsion containing, in aqueous medium, from 0.25% to 2.0% of a water-insoluble, oil-soluble polar substances such as alkylated or alkenylated succinic acids or anhydrides or mixtures of such substances and other oils, from 5% to 25% of a water-soluble polar organic compound or mixtures of such compounds, and enough water to make a 50% float. The amount of each ingredient is based on the wet drained weight of wet leather to be lubricated. The water-soluble, polar organic compound serves only to disperse the water-insoluble, oil-soluble polar substances or such substances and other oils throughout the aqueous medium to produce an emulsion and is not absorbed into the hide or leather being lubricating but remains behind in the float.

A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This application is a continuation-in-part of our co-pending application for patent, Ser. No. 880,432 filed Nov. 26, 1969, now abandoned, which in turn is a continuation-in-part of application for patent, Ser. No. 482,639, filed Aug. 25, 1965, and now abandoned.

This invention relates to lubrication of leather. More particularly, this invention relates to a new process for lubricating leather with water-insoluble, oil-soluble polar substances such as alkylated or alkenylated succinic acids or anhydrides, hereinafter referred to as ASA, of the type



where R is alkyl or alkenyl of twelve or more carbon atoms. The alkenyl succinic acids and/or anhydrides are available by interaction of a long chain α-olefin with maleic anhydride or maleic acid. Hydrogenation of these materials produces the alkyl succinic acids and/or anhydrides. In actual commerce pure α-olefins may not be used, hence mixtures are often produced with a preponderance of a particular chain length. In our invention reaction products where R is alkyl or alkenyl of twelve or more carbon atoms have been found operative. However, in our invention we prefer alkenyl or alkyl succinic acids in which R contains on the average eighteen carbon atoms.

An object of the present invention is to provide a process

for lubricating leather with very small amounts of lubricant.

Another object is to provide a process for lubrication of leather that can be carried out in conventional equipment and by conventional processes commonly used in fat-liquoring of leather.

A further object of this invention is to describe a practical and inexpensive process for lubrication of leather with an alkyl or alkenyl substituted succinic acid, or derivative thereof.

Another object of the invention is to provide a process for lubricating leather so that on drying a soft, mellow leather results without the need for a staking operation.

Another object of the invention is to provide a process for lubricating leather so that the leather lends itself to efficient water repellent processes.

A further object of this invention is to provide a process for lubricating mineral tanned leather or leather tanned with a combination of a mineral tanning agent and an organic tanning agent such as vegetable tans, aldehydes, syntans, resins, etc., with an alkyl or alkenyl succinic acid.

When unlubricated wet leather, such as chrome leather "in the blue," is allowed to become dry it becomes hard and stiff and difficult to process further. For this reason chrome leather is not dried or brought to the "crust" stage until after it is lubricated. In the crust chrome leather is stiff, but it can be readily hyrated for further processing, one such process being staking. In commercial practice lubrication is by means of fat liquors with one or more surface active agents. The process is usually conducted by drumming the tanned stock with the fat liquor, which is an oil-in-water type emulsion at an elevated temperature, generally 45–55° C., for about a half hour. Usually the lubricant is exhausted from the treating bath and enters the leather fibers. This general procedure has been used by the leather tanners for many years.

Recently, G. H. von Fuchs (British Pat. 925,174; JALCA, 52, 550–559, October 1957) proposed a novel method for lubricating leather. This method comprises wringing the chrome-tanned leather to reduce the moisture content to between 45% and 60% and then dipping the wrung leather in a mineral spirits solution of an alkyl or alkenyl succinic acid. This method has several disadvantages. In the first place the water content is a critical and important factor. Secondly this process must be effected as a dipping process. Attempts to apply the Von Fuchs' process to lubrication of leather in a drum were to no avail. A thick gelatinous mass was formed that remained on the surface of the leather or clung to the surfaces of the drum. Little penetration of the ASA into the fiber resulted, and no lubrication was effected. The ASA remained completely in the aqueous gelatinous mass.

We have discovered how to prepare an aqueous emulsion of ASA, either alone or in the presence of other oils, that can be incorporated into chrome leather in conventional equipment as used in a conventional fat-liquoring process. The aqueous emulsion was achieved by including in the mixture a water-soluble, polar organic compound or mixtures of such compounds. Only a minor amount of water-soluble compound is needed, less than 25% of the amount of water taken as dispersing medium. The purpose of the water-soluble, polar organic compounds is to disperse the ASA or ASA and vegetable or animal oil to produce an oil-in-water type emulsion from which the ASA or ASA and oil can be absorbed into the hide or leather fibers without depositing in the fibers the water-soluble, polar organic compound. Dispersions can be made of

liquid or solid ASA and ASA's containing sixteen or more carbon atoms in the substituted alkyl or alkenyl succicic acid.

In a preferred embodiment of the invention, leather is lubricated by a process comprising impregnating unlubricated wet leather with an aqueous emulsion consisting essentially of about from 5 to 25%, based on wet drained weight of the leather of a relatively non-volatile, water-soluble, polar organic compound or mixtures thereof and from about 0.25 to 2.0% ASA, based on wet drained weight of the leather, in sufficient water to provide an adequate float for distributing the emulsion through the leather.

It has been found that in the emulsified state the ASA emulsion is rapidly and efficiently absorbed by the leather and the process can be effectively carried out in a drum. No emulsifying agents such as soaps, sulfated oils, etc., need be added. Moreover, by the process of the instant invention, raw oils can be used with the ASA to give emulsions that can be satisfactorily used for fat-liquoring leather. The amount of ASA and/or oil are not critical. We prefer to use about 1% of ASA and/or 5% of raw vegetable or animal oil; however, lesser or greater amounts of these may be used depending on the type of leather desired.

Unless otherwise stated the emulsions of this invention contained sufficient water to make a 50% float, based on the wet drained weight of the wet leather to be lubricated, that is, the combined weight of the ASA or ASA and other oils, the water-soluble, polar organic compound and the water added to make the float was equal to 50% of the weight of the wet drained leather being treated. The wet drained weight of the leather, which is fairly constant for each type of animal skin, is that weight after the chrome tanned leather has been horsed and allowed to drain.

An important feature of this invention is that although the water-soluble, polar organic compound is an important factor in the preparation of the emulsion in which ASA and other oils are incorporated, it is not part of the actual lubrication process of this invention.

In addition to the fact that the process of this invention can be carried out in conventional fat-liquoring process equipment, a very important facet of the invention is that the emulsion is completely exhausted of the ASA or ASA plus other oils while the water-soluble polar organic compound remains behind in the float. Thus, the amount of oil that one desires to incorporate into the leather can be easily controlled merely by putting the desired amount into the emulsion.

The fact that the emulsion is completely exhausted of ASA or ASA plus other oils and that no measurable amount of the water-soluble polar organic compound is deposited in the leather was demonstrated by reextracting the fat out of the leather. In all cases, regardless of the amount or combination of oils used the reextracted fat equaled that used in the emulsion showing that all the ASA or ASA plus other oils and only the ASA or ASA plus other oils is being removed from the emulsion. As seen in Table I the amount of chloroform extractables is very close to the combined amount of ASA or neatsfoot oil in the lubricating emulsion. This shows clearly that the THFA was not absorbed by the leather but remained in the float, especially in view of the fact that tetrahydrofurfuryl alcohol (THFA) is infinitely soluble in chloroform.

Although typically applied to the leather in a volume representing a 50% float, larger or smaller volumes of emulsion may be used. Since the emulsions persist with widely varying dilutions in water, the important feature for efficient lubrication of the leather is that the ASA be dispersed in sufficient water to provide an adequate float for uniform distribution of the emulsion throughout the unlubricated leather.

TABLE I

THFA [1], percent	Fat liquor combination: ASA, percent	Fat liquor combination: Neatsfoot oil, percent	Chloroform [1] extractables (wet basis) percent
5	0.25	1.0	1.44
5	0.25	2.0	2.28
5	0.50	2.0	2.60
5	0.50	4.0	4.28
10	0.25	2.0	2.32
10	0.25	4.0	4.16

[1] Based on wet drained weight of leather.

No special treatment need be given to the tanned stock to prepare it for the lubrication process of the present invention. Chrome-tanned leather in the blue (after neutralization to set the chrome tan) can be used directly without adjusting the pH of the stock. The lubrication process can be applied to any mineral-tanned stock such as chrome, alum, or zirconium tanned hides or skins. Likewise it may be applied to stock tanned with organic tanning agents such as vegetable tannins, aldehydes, epoxides, isocyanates, etc., or to hides and skins tanned with a combination of mineral and organic tanning agents. Especially preferable in our process is chrome-tanned leather. This may be used after neutralization of the chrome tannage as mentioned above, or if preferred, it can be processed further such as retanned with vegetable tannins, glutaraldehyde, etc., or it may be colored prior to application of our lubrication process.

The water content of the stock is not critical in our process. The tanned stock may vary from a comparatively dry stock (i.e. wrung) to one that is soaking wet. We prefer to operate our invention at a somewhat elevated temperature, preferably about 40–55° C., although temperatures below 40° C. or higher than 55° C. may be employed. In the temperature range of 40–55° C. the emulsion is exhausted in less than one hour.

Various water-soluble, polar organic compounds can be used as dispersants in this invention. Volatile solvents of this class such as acetone, isopropyl alcohol, methanol and ethanol serve to function as dispersing agents for the ASA and permit complete exhaustion of the ASA. The leather is, however, stiff, and these solvents are not preferred for the purposes of this invention.

Preferred compounds are the relatively less volatile water-soluble polar substances such as alkylene glycols and their ether and/or ester derivatives, polyalkylene glycols and their ether and/or ester derivatives, and ether and keto alcohols. These include tetrahydrofurfuryl alcohol, diacetone alcohol, ethylene and polyethylene glycols, propylene and polypropylene glycols, polypropylene glycol methyl ethers, glycol and polyalkylene glycol monoethers, glycol and polyalkylene glycol diethers, and glycol and polyalkylene glycol monoether monoesters.

Specific compounds operative in the invention include the glycols: dipropylene glycol, tetraethylene glycol, Carbowax 300, Carbowax 400, Carbowax 550, and hexylene glycol. Also included are the ether alcohols: diethylene glycol monomethyl ether (methyl Carbitol), diethylene glycol monoethyl ether (Carbitol), diethylene glycol monobutyl ether (butyl Carbitol), ethoxy triglycol, methoxy-triglycol, and tetrahydrofurfuryl alcohol. Ethers and esters include diethylene glycol diethyl ether, Cellosolve acetate, Carbitol acetate and dipropylene glycol methyl ethers. Also operative in the invention is diacetone alcohol.

In the practice of our invention a minor proportion, relative to water, of the water-soluble polar organic compound is used. Any of the well-known methods for producing emulsions may be used. A convenient practice is to dissolve the ASA in the water-soluble polar solvent and then the water with stirring. One may add raw vegetable or animal oil to the ASA if one so desires.

Practice of some preferred embodiments of the invention are demonstrated in Examples 1–5, 7–8, and 13–26, but are not intended to be in limitation of the scope

of the invention. Example 6 serves to illustrate the critical significance of ASA in the leather lubricating systems. Examples 9 to 12 are included to illustrate the results obtained with volatile, low molecular weight, polar organic solvents.

EXAMPLE 1

Specimens of commercial chrome-tanned grain split leather in the blue were fat-liquored with emulsions consisting of ¼, ½, 1 or 2% of alkenyl acid (ASA), 5% tetrahydrofurfuryl alcohol (THFA) based on the drained weight of the leather and sufficient water to give a 50% float. The emulsion was prepared by warming the ASA in the tetrahydrofurfuryl alcohol and dissolving to a clear solution. The required amount of water at 50° C. was added with stirring to the solvent mixture whereupon an emulsion was formed. Fat-liquoring of the wrung leather was carried out in the conventional manner maintaining the temperature of the fat-liquoring system at 50° C. Complete exhaustion of the fat-liquor was obtained in each instance in less than one hour. No adjustment of the system such as addition of acetic acid or salt to break the emulsion was required to reach complete exhaustion of the emulsion.

EXAMPLE 2

The procedure of Example 1 was followed with the exception that the tetrahydrofurfuryl alcohol was raised to 10% based on the drained blue weight of the stock. Complete exhaustion of the fat liquor was obtained in less than one hour.

EXAMPLE 3

The procedure of Example 1 was followed with the exception that the tetrahydrofurfuryl alcohol was raised to 15% based on the drained blue weight of the leather. Complete exhaustion of the fat liquor was obtained in less than one hour.

EXAMPLE 4

The procedure of Example 1 was followed with the exception that the tetrahydrofurfuryl alcohol was raised to 25% based on the drained weight of the leather Complate exhaustion of the fat liquor was attained in less than one hour.

EXAMPLE 5

The specimen of chrome-tanned grain split leather was retanned with 5 or 10% glutaraldehyde (25% solution) as described by recommended procedures. The retanned leather was fat-liquored in accordance with Examples 1–4 where ¼, ½, 1 or 2% of ASA and 5, 10, 15 and 25% tetrahydrofurfuryl alcohol were used, respectively, based on the drained weight of the leather. Emulsions thus formed with water were easily exhausted in less than one hour resulting in leathers that were flexible and soft, even softer than the chrome grain splits (Example 4), which were not retanned. This shows that the invention is operative with various tannages.

EXAMPLE 6

An attempt was made to fat-liquor with raw oils without the use of ASA following the general procedure outlined in Example 1. Based on the wrung blue weight, 2% neatsfoot oil was dissolved by warming in 5% of tetrahydrofurfuryl alcohol. The blue stock was added to the warm solution and churned under heat (about 50° C.) for 30 minutes. Sufficient warm water (50° C.) was added to give a 50% float and churning at a temperature of 50° C. was continued an additional hour. No emulsion was formed and little fat-liquoring was attained by this system since globules of oil were visible on the walls of the jar and on the grain of the leather. Similar results were obtained even when the neatsfoot oil content was increased up to 6% and the THFA increased to 20% based on the wrung blue weight. That it is clear that in the absence of ASA fat-liquoring or absorption of oil was not attained.

EXAMPLE 7

The procedure of Example 6 was repeated except for the fact that 0.5% (based on the blue weight) of Casyl 18, an alkenyl succinic acid containing on the average a total of 22 carbon atoms (R=18 in above general formula), was also added to the neatsfoot oil when dissolved in the THFA. A very nice emulsion was formed when water at 50° C. was added to the solution of ASA and neatsfoot oil in THFA. Chrome-tanned stock warmed to 50° C. was added and churned while maintaining the temperature at 50° C. for one hour. Complete exhaustion of the fat liquor was attained as evidenced by clearing of the emulsion. Evidence as to complete exhaustion was also demonstrated by extracting the dried leather with chloroform. Extracted fat was equivalent to the total fat used in fat-liquoring the wet leather. Substantially similar results were obtained with higher or lower amounts of ASA, higher amounts of THFA and/or different types or amounts of raw oils, such as safflower, cod, soybean, and castor oil.

This compared to Example 6 shows the need for ASA to produce emulsions with raw oil useful for fat-liquoring.

EXAMPLE 8

The procedure for Example 7 was followed with the exception that the chrome stock in the blue was retanned with glutaraldehyde before fat-liquoring. As in Example 7 the fat liquor was completely exhausted, and a mellow leather resulted.

EXAMPLE 9

A sample of a chrome grain split leather retanned with 10% glutaraldehyde (25% solution) was fat-liquored with 1% alkenyl succinic acid (ASA) dissolved with slight heating in 10% acetone (all percentages based on the wet wrung weight of the leather). The required amount of water, 40% based on the wrung weight, heated to 50° C., was added to the ASA-solvent system and stirred. In this case a light emulsion was formed. The warm wet wrung leather was placed in the fat-liquoring system and churned for one hour under heat at approximately 50° C. Exhaustion of the fat liquor was atttained in one hour with temperature of the exhausted system at approximately 40–42° C. Leather fat-liquored with this system dried out rather stiff.

EXAMPLES 10–12

The procedure of Example 9 was followed with the exception that 10% (based on the blue weight) of methanol (Example 10), ethanol (Example 11) and isopropyl alcohol (Example 12) were used in the separate examples in place of the 10% acetone. The dried leathers in the crust were stiff. These examples show that volatile organic solvents such as acetone, methanol, and isopropyl alcohol are not effective to produce the desired flexible, mellow lubricated leathers.

EXAMPLES 13–26

The procedure of Example 9 was followed with the exception that 5 to 10% (based on blue weight) of one of the following water-soluble organic substances of comparatively low volatility was used in each example in place of the acetone: diethylene glycol monobutyl ether (Example 13), diethylene glycol monomethyl ether (Example 14), diethylene glycol diethyl ether (Example 15), diethylene glycol monoethyl ether (Example 16), the acetate of diethylene glycol monoethyl ether (Carbitol acetate) (Example 17), polyethylene glycol (Carbowax 400) (Example 18), dipropylene glycol (Example 19), tetraethylene glycol (Example 20), hexylene glycol (Example 21), ethoxytriglycol (Example 22), propylene glycol monomethyl ether (Example 23), dipropylene glycol methyl ether (Example 24), tripropylene glycol methyl ether (Example 25), and diacetone alcohol (Example 26). The unstaked dried leather; i.e., the leather in the

crust, from each of the above examples was flexible and mellow, comparable to crust leather after it has been mechanically staked.

Combinations of two or more of the relatively non-volatile, water soluble, polar organic compounds have also been used, particularly combinations in which one of the solvents is tetrahydrofurfuryl alcohol and/or diethylene glycol monobutyl ether, to give flexible, mellow lubricated leather.

The statement "complete exhaustion of the fat-liquor" as used in the specifications means that only the ASA or ASA plus other animal or vegetable oils was absorbed into the leather from the emulsion and that the water-soluble polar organic compounds remained in the float.

We claim:

1. A fat-liquor emulsion for treating hides and leathers comprising, in aqueous medium:

(a) about from 0.25% to 2.0%, based on the wet drained weight of wet leather to be treated, of a lubricant selected from the group consisting of compounds of the formula $RCH(CH_2CO_2H)CO_2H$ wherein R is selected from the group consisting of long chain alkenyl radicals containing from 12 to 18 carbon atoms, and mixtures of said compounds and other oils;

(b) about from 5% to 25%, based on the wet drained weight of wet leather to be treated, of a water-soluble, polar organic compound selected from the group consisting of diethylene glycol monomethyl ether, diethylene glycol monethyl ether, diethylene glycol monobutyl ether, diethylene glycol diethyl ether, dipropylene glycol, dipropylene glycol monomethyl ether, dipropylene glycol dimethyl ether, tripropylene glycol methyl ether, tetraethylene glycol, a polyethylene glycol having an average molecular weight in the range of about from 285 to 600, hexylene glycol, ethoxy triglycol, methoxytriglycol, diacetone alcohol, tetrahydrofurfuryl alcohol, ethylene glycol monobutyl ether acetate, diethylene glycol monobutyl ether acetate and mixtures thereof, said water-soluble, polar organic compound functioning only to disperse the aforesaid lubricant throughout the aqueous medium to produce the emulsion; and

(c) enough water to make a 50% float based on the wet drained weight of the leather to be treated;

said fat-liquor emulsion being unique in that, when applied to hides and leathers, it is completely exhausted of and deposits on said hides and leathers only the lubricant while leaving the water-soluble polar organic compound in the float.

2. The fat-liquor emulsion of claim 1 in which the water-soluble, polar organic compound is diethylene glycol monobutyl ether.

3. The fat-liquor emulsion of claim 1 in which the water-soluble, polar organic compound is tetrahydrofurfuryl alcohol.

4. The fat-liquor emulsion of claim 1 in which the water-soluble, polar organic compound is a polyethylene glycol having an average molecular weight of about 300.

5. The fat-liquor emulsion of claim 1 in which the water-soluble, polar organic compound is diacetone alcohol.

6. The fat-liquor emulsion of claim 1 in which the water-soluble, polar organic compound is tripropylene glycol methyl ether.

References Cited

UNITED STATES PATENTS

3,291,557	12/1966	Neher et al.	8—94.23
2,974,000	3/1961	Retzsch et al.	8—94.23
2,693,996	11/1954	Von Fuchs	8—94.23
2,208,809	7/1940	Johnson et al.	69—21
2,158,627	5/1939	Kritchevsky	8—94.21

FOREIGN PATENTS

101,474	11/1936	Australia	8—94.21
925,174	5/1963	Great Britain	8—94.23
964,994	7/1964	Great Britain	8—94.23

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