United States Patent Office 3,010,780 Patented Nov. 28, 1961

3,010,780
METHOD OF MAKING LEATHER WATER-REPELLENT

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No Drawing. Filed Mar. 25, 1958, Ser. No. 723,659
Claims priority, application Germany Mar. 30, 1957
11 Claims. (Cl. 8—94.26)

This application is a continuation-in-part of copending application Serial No. 550,212, filed November 30, 1955, now abandoned.

This invention relates to a method of making leather water-repellent.

Broadly stated, we have found that leather is rendered water-repellent by depositing within the tanned animal hide a complex compound formed by a mineral-tanning agent with a tribasic or higher polybasic acid derivative containing a hydrophobic group. The term "hydrophobic group" as used herein is well known in the chemical arts and has been defined by Schwartz and Perry in their publication "Surface Active Agents," Interscience Publishers, Inc., New York (1949), on pages 17–19 as follows:

"In view of these considerations it is important to examine some of the more usual types of hydrophobic groups and the ways in which they are obtained.

"(1) The straight alkyl chains of eight to eighteen or more carbon atoms are derived from the natural fatty acids. These may be used as such or may be converted to acid chlorides for use in acylation reactions. The acids or their esters may also be reduced to the corresponding fatty alcohols or through the nitriles to the fatty amines. These in turn can be used as intermediates in a variety of reactions to introduce the long alkyl chain. The natural fatty acids are possibly the most important raw material for hydrophobic groups. A wider variety of detergents has been derived from them directly or indirectly, than from any other single source.

"(2) The lower alkyl groups of three to eight carbon atoms are frequently attached to aromatic nuclei such as benzene or naphthalene, the combination forming a useful type of hydrophobic group. The sources of lower alkyl groups are usually the alcohols. The lower alkyl groups are sometimes used by themselves as hydrophobic groups, as in the case of the dialkyl sulfosuccinates: . . .

"(5) Certain types of petroleum yield naphthenic acids in the normal course of refining. These are surface active in themselves and have also been used as a source of hydrophobic groups in derived surface active agents. In the refining of petroleum oils by washing with sulfuric acid the surface active petroleum sulfonates are obtained."

More particularly, we have found that water-repellent leather is obtained by either of two methods:

(1) By impregnating a mineral-tanned or combination synthetic resin-mineral- or vegetable-mineral-tanned animal hide with a water-soluble or water-dispersible organic compound which will combine in situ with the mineral-tanning agent already present in the hide to form water-repellent complexes.

(2) By impregnating vegetable-tanned or synthetic resin-tanned animal hide with a water-soluble or water-dispersible organic compound which will combine in situ with a mineral-tanning agent to form water-repellent complexes, and thereafter providing the necessary mineral-tanning agent by retanning the hide with a mineral-tanning agent.

In either case, the mineral-tanning agent furnishes the ion for the formation of the complex compound in situ in the tanned hide. Examples of particular mineral-tanning agents are chrome-, aluminum- and iron-tanning agents. Among aluminum-tanning agents, basic aluminum salts, and especially aluminum sulfate and alum, are particularly suitable.

In general, organic compounds which we have found to be suitable for this purpose are derivatives of tribasic or higher polybasic inorganic or organic acids which contain hydrophobic radicals and at least two free, salt-forming groups capable of combining with the mineral-tanning agent to form an organometallic complex grouping. Such polybasic acid derivatives have acid characteristics and are preferably used for the purpose set forth in the form of their water-soluble salts, especially those formed by neutralization with organic bases, their ammonium salts and alkali metal salts.

Examples of suitable inorganic polybasic acids upon which the above derivatives are based are boric acid, phosphoric acid, arsenic acid and the like. Similarly suitable organic polybasic acids are, among others, citric acid, trimesitinic acid, trimellitic acid, mellitic acid, diadipic acid, ethane-tetraacetic acid, sulfophthalic acids, oxyphthalic acids, pyrogallic acid, pyrogallol carboxylic acids, and the like. Other suitable organic acids are those which contain hydrophobic radicals and may, for example, be obtained by subjecting high molecular weight unsaturated fatty acids, fatty alcohols or olefins to a condensation reaction with maleic acid, such as the condensation products of oleic acid, linseed oil fatty acid, soybean oil fatty acid, and the like, with one or several mols of maleic acid.

While the above high molecular weight tribasic or higher polybasic carboxylic acids may be used without modification to form organometallic complex compounds with the mineral-tanning agent, the tribasic or higher polybasic inorganic acids or the low molecular weight tribasic or higher polybasic carboxylic acids disclosed above are preferably transformed into compounds having an affinity to form complexes with the mineral-tanning agent, by partial esterification or partial amidation with high molecular alcohols or amines, respectively. The resulting products are either well-known materials or are readily obtainable by methods known in the art. In place of these particular compounds, any other suitable compounds may be used, provided they contain at least one hydrophobic radical and at least two salt-forming radicals capable of forming complexes with the mineral-tanning agent.

Examples of some specific compounds which are capable of forming complexes with the mineral-tanning agent and which may be used to increase the water-impermeability of leather in accordance with the present invention are the following: acid dodecylphosphate, acid octadecenylphosphate, hexadecylborate, octadecenylarsenate, hexadecylcitrate, acid dodecylsulfophthalate, citric acid mononaphthenyl amide, citric acid monooctadecyl amide, and the like. Such compounds may be employed as such or in the form of their water-soluble salts.

The hydrophobic radicals of these compounds may be of an aliphatic, cycloaliphatic, aliphatic-aromatic or aliphatic-cycloaliphatic nature, and may be interrupted by oxygen, nitrogen or sulfur atoms or carry substituent radicals comprising oxygen, sulfur or nitrogen atoms. Of particular interest are, for example, tribasic or higher polybasic organic or inorganic acids esterified with high molecular weight ethoxylated fatty alcohols, especially high molecular weight fatty alcohols ethoxylated with 1 to 10 mols, preferably 1 to 3 mols, of ethyleneoxide per mol of alcohol.

The waterproofing treatment of leather with aqueous solutions or dispersions of these compounds is carried out in accordance with the usual procedures; for ex-

ample, by immersion of the leather in the solution or dispersion, or by brushing the solution or dispersion onto the leather. The amount of such compounds which is generally required to achieve the desired waterproofing effect ranges from 0.5 to 15%, based upon the shaved weight of the leather, but amounts from 1.5 to 5% are preferred.

The polybasic acid derivatives used in accordance with this invention inherently possess fatting properties. Consequently, depending upon the quantity of such derivatives used, the leather need not be fat-liquored at all or the amount of fat-liquoring agent applied to the leather can be substantially curtailed.

A further improvement of the water-repellent properties of leather can be achieved by employing the polybasic acid derivatives herein disclosed, slightly in excess, and thereafter treating the leather with small quantities of a commercial mineral-tanning agent, fat-liquoring and finishing in the customary manner. This subsequent treatment of the waterproofed leather with small amounts of mineral-tanning agent renders still soluble components which may have been absorbed by the leather insoluble. In other words, this treatment assures that all of the polybasic acid derivative available to form metal complexes has been transformed into such water-repellent complexes.

Another method of improving the water-repellent characteristics of the leather impregnated in accordance with the present invention is heating the finished and dried leather to temperatures up to about 90° C. for extended periods of time.

As previously mentioned, the water-proofing treatment described herein may also be applied in conjunction with a combination vegetable-and-mineral-tanning procedure. For example, a vegetable-tanned leather may be first treated with the hydrophobic polybasic compounds and subsequently treated with mineral-tanning agents. Hence, it is possible to achieve vegetable or combination tanning effects along with the water-repellent effect, depending upon the amount of vegetable- and mineral-tanning agents employed.

The waterproofing treatment according to the present invention may be applied to all types of mineral-tanned and combination-tanned leather, and is particularly advantageous when used in conjunction with suede leather whose water-repellent characteristics are often unsatisfactory. The waterproofing treatment increases the water-permeability quotient of untanned skins in most cases by 100%, for example to about 1.8, while the normal water-absorption capacity is reduced by about one-half, without, however, impairing the air-permeability of the leather. Another particular advantage of the process according to the present invention is that it permits the manufacture of light-colored, particularly white aluminum-tanned leather having extraordinary water-repellent properties.

The following examples will further illustrate the present invention and enable others skilled in the art to understand it more completely. We wish it to be understood, however, that we do not intend to limit ourselves to the particular compounds and conditions recited in these examples.

Example I

Chrome-tanned and neutralized cow hides were immersed for 45 to 60 minutes at a temperature of 50° C. in a solution consisting of 100 to 150% water and 1 to 5% of the ammonium salt of an acid phosphoric acid dodecyl ester, based upon the shaved weight of the hides being treated. Subsequently, the impregnated leather was dyed in the customary manner and fat-liquored with a commercial fat-liquoring agent to achieve the desired suppleness. The leather was then finished in the customary manner. The resulting leather was not only of high quality but also showed improved water-repellent characteristics.

Example II

Chrome-tanned, dyed and neutralized cow hides were immersed in the waterproofing solution as described in Example I. Thereafter, the impregnated leather was chrome-tanned in a separate vessel with a commercial chrome-tanning agent containing 0.5 to 1% Cr_2O_3, fat-liquored and finally dried in the customary manner. The water-repellent properties of the resulting finished leather were even more improved than those of the leather obtained in Example I.

Similar results were obtained when the dry finished leather of Example I was heated to about 90° C. for 45 minutes to 1½ hours.

Example III

Bark-tanned cow hides were immersed for 45 to 60 minutes in a solution consisting of 100 to 150% water at 50° C. and 1 to 5% of the ammonium salt of the monooleyl ester of citric acid, based upon the shaved weight of the hides being treated. Thereafter, the impregnated leather was chrome-tanned with 0.5 to 1% Cr_2O_3 in the form of a commercial 33% basic chrome-tanning agent, fat-liquored and then finished in the customary manner. The resulting leather is of high quality and has excellent water-repellent characteristics.

Example IV

Chrome-tanned and neutralized calf skins were immersed for 45 to 60 minutes in an aqueous solution consisting of 100 to 150% water and 1 to 5% of the ammonium salt of the condensation product obtained by condensing 1 mol linseed oil fatty acid and 1 to 2 mols maleic acid. Thereafter, the impregnated leather was finished as described in Example I. The resulting leather was also of high quality and had excellent water-repellent properties.

Example V

1 to 5% of the ammonium salt of the acid diadipic acid didodecylester was used instead of the ammonium salt of an acid phosphoric acid dodecylester in Example I. A high quality leather having good water-repellent properties was obtained.

Example VI

1 to 5% of the ammonium salt of the acid sulfophthalic monooctadecenylester was used instead of the ammonium salt of an acid phosphoric acid dodecylester in Example I. A high quality leather having good water-repellent properties was obtained.

Example VII

1 to 5% of the sodium salt of the acid oxyphthalic acid octadecylester was used instead of the ammonium salt of an acid phosphoric acid dodecylester in Example I. A high quality leather having good water-repellent properties was obtained.

Example VIII

1 to 5% of the ammonium salt of the acid arsenic acid mononaphthenylester was substituted for the ammonium salt of the monooleylester of citric acid in Example III. An excellent water-repellent leather was obtained.

Example IX

1 to 5% of the ammonium salt of the acid ethanetetraacetic acid monooctadecylester was substituted for the ammonium salt of the monooleylester of citric acid in Example III. An excellent water-repellent leather was obtained.

Example X

1 to 5% of the ammonium salt of the citric acid monododecylamide was substituted for the ammonium salt of the monooleylester of citric acid in Example III. An excellent, highly water-repellent leather was obtained.

Example XI

1 to 5% of the ammonium salt of the condensation product from 1 mol soyabean oil fatty acid and 1 to 2 mols maleic acid was used instead of the ammonium salt of the condensation product from 1 mol linseed oil fatty acid and 1 to 2 mols maleic acid of Example IV. A leather was obtained which had good water-repellent properties.

Example XII

1 to 5% of the ammonium salt of the trimellitic acid monooctadecylamide was used instead of the ammonium salt of the condensation product from 1 mol linseed oil fatty acid and 1 to 2 mols maleic acid of Example IV. A leather was obtained which had good water-repellent properties.

Example XIII

Aluminum-tanned and neutralized sheep hides were soaked for 45 to 60 minutes in a drum containing 100 to 150% water at 50° C. and from 1 to 5% of the ammonium salt of an acid phosphoric acid monododecylester, both percentages being based upon the shaved weight of the hides. Subsequently, the impregnated hides were removed from the drum and dyed in the customary fashion, and then fat-liquored with a commercial fat-liquoring oil to achieve the desired suppleness. The leather may, however, also be dyed prior to the impregnation with the phosphoric acid ester salt. The leather obtained thereby was extremely supple and had very pure color tones. In addition, the finished leather had excellent water-repellent properties. The water-repellent effect was further increased when, subsequent to the treatment with the acid phosphoric acid ester salt, the hides were retanned in a separate bath with 0.5 to 1% Al_2O_3 (commercial aluminum or alum tanning agent), fat-liquored and dried in the customary fashion. The water-repellent properties of the leather were further increased by heating the dried leather for about 45 minutes to 1½ hours at about 90° C.

Example XIV

Delimed and bated sheep skins which had been degreased to the desired degree were soaked in 100% water at 20° C. in a rotating drum. From 0.5 to 1.5% formaldehyde were added in small portions to the soaking water and after 15 to 30 minutes the pH of the soaking solution was slowly adjusted to between 8 and 8.5. Total running time: 1 to 2 hours. The tanned pelts were then stored overnight on the horse and the following morning they were retanned with 1% Al_2O_3 in the form of a basic commercial aluminum tanning agent or with potassium aluminum alum (100% solution; running time: about 1½ hours). Prior to the retanning step, the pelts may also be soaked for some time in an acid solution or in a weak formic acid pickling bath. After rinsing the aluminum-tanned pelts and neutralizing them, they were impregnated with 1 to 5% of the ammonium salt of an acid phosphoric acid monododecylester. The impregnation effect was further improved by retanning the skins in a separate bath with 0.5 to 1% Al_2O_3 in the form of a commercial aluminum tanning agent or potassium aluminum alum. All of the above percentages are based upon the shaved weight of the skins. After fat-liquoring to the desired degree and drying the skins in the customary fashion, a white, soft, supple, light-stable leather was obtained which also exhibited excellent water-repellent properties.

Example XV

Leather completely tanned with light natural tanning agents or synthetic white tanning agents was either dyed with light pastel dyes or was allowed to remain white. Thereafter it was soaked in a solution containing from 1 to 5% of the ammonium salt of a high-molecular-weight polycarboxylic acid which had been obtained by the reaction of 1 mol linseed oil fatty acid with 1 to 2 mols maleic acid. The impregnated leather was then treated as described in Example XIII and retanned with from 0.5 to 1% Al_2O_3. The retanned leather was then fat-liquored with a commercial fat-liquoring oil to the desired degree of suppleness. A white or pastel-colored, supple, light-fast leather was obtained, which also exhibited excellent water-repellent properties. The above percentages are also based upon the shaved weight of the skins.

Example XVI

White leather tanned with melamine resin or dicyandiamide resin was rinsed and then soaked in a solution containing 100 to 150% water at 50° C. and 1 to 5% of the ammonium salt of an acid phosphoric acid monododecylester (running time: 40 to 60 minutes). Thereafter the skins were retanned in a separate bath containing 80 to 100% water and 0.5 to 1% Al_2O_3 in the form of a commercial aluminum tanning agent or potassium aluminum alum (running time: about 2 hours). The retanned leather was then fat-liquored as needed to the desired degree of suppleness and dried in the customary fashion. The water-repellent effect was increased by subjecting the dried leather to temperatures of about 90° C. for a short period of time. A white, water-repellent apparel leather was obtained.

While we have illustrated our invention with various specific embodiments, it will be obvious to persons skilled in the art that various changes and modifications may be made without departing from the spirit of the invention or the scope of the appended claims.

We claim:

1. The method of making tanned animal hides water-repellent, which comprises impregnating said hides with a complex organometallic compound formed by interaction in situ of (1) an a anionic water-miscible compound selected from the group consisting of (*a*) esters and amides of tricarboxylic and higher polycarboxylic organic acids and tribasic and higher polybasic inorganic acids, said esters and amides containing at least one organic hydrophobic waterproofing radical in the ester and amide moiety and (*b*) condensation products of high molecular weight unsaturated fatty acid with maleic acid, said compound containing at least two free, salt-forming groups capable of forming an organometallic complex with metallic ions in the mineral-tanning agent, and (2) a mineral-tanning agent selected from the group consisting of chrome-, aluminum- and iron-tanning agents, and drying the impregnated hides.

2. The method of making mineral-tanned animal hides water-repellent, said hides being tanned with a mineral-tanning agent selected from the group consisting of chrome-, aluminum-, and iron-tanning agents, which comprises impregnating said hides with an anionic water-miscible compound selected from the group consisting of (*a*) esters and amides of tricarboxylic and higher polycarboxylic organic acids and tribasic and higher polybasic inorganic acids, said esters and amides containing at least one organic hydrophobic waterproofing radical in the ester and amide moiety and (*b*) condensation products of high molecular weight unsaturated fatty acid with maleic acid, said compound containing at least two free, salt-forming groups capable of forming an organometallic complex compound with said mineral-tanning agent, and drying the impregnated hides.

3. The method of making mineral-tanned animal hides water-repellent, said hides being tanned with a mineral-tanning agent selected from the group consisting of chrome-, aluminum-, and iron-tanning agents, which comprises impregnating said hides with an anionic water-soluble salt of a polybasic acid ester of a tribasic inorganic acid, said acid ester being esterified with high molecular weight fatty alcohols and said acid ester containing at least two free, salt-forming groups capable of forming an organometallic complex compound with said

mineral-tanning agent, and drying the impregnated hides.

4. The method of making mineral-tanned animal hides water-repellent, said hides being tanned with a mineral-tanning agent selected from the group consisting of chrome-, aluminum-, and iron-tanning agents, which comprises impregnating said hides with an anionic water-soluble salt of an at least tricarboxylic organic polycarboxylic acid ester, said acid ester containing organic hydrophobic waterproofing radicals and said acid ester containing at least two free, salt-forming groups capable of forming organometallic complex compounds with said mineral-tanning agent, and drying the impregnated hides.

5. The method of making mineral-tanned animal hides water-repellent, said hides being tanned with a mineral-tanning agent selected from the group consisting of chrome-, aluminum-, and iron-tanning agents, which comprises impregnating said hides with an anionic water-soluble salt of an at least tricarboxylic organic polycarboxylic acid amide, said acid amide salt being derived from an amine containing hydrophobic alkyl radicals and said acid amide salt containing at least two free, salt-forming groups capable of forming organometallic complex compounds with said mineral-tanning agent, and drying the impregnated hides.

6. The method of making mineral-tanned animal hides water-repellent, said hides being tanned with a mineral-tanning agent selected from the group consisting of chrome-, aluminum-, and iron-tanning agents, which comprises impregnating said hides with an anionic water-miscible compound selected from the group consisting of (*a*) esters and amides of at least tricarboxylic organic acids and at least tribasic inorganic acids, said esters and amides containing at least one organic hydrophobic waterproofing radical in the ester and amide moiety and (*b*) condensation products of high molecular weight unsaturated fatty acid with maleic acid, said compound containing at least two free, salt-forming groups capable of forming an organometallic complex compound with said mineral-tanning agent, the amount of said water-miscible compound being in excess of that required to combine with all of said mineral-tanning agent in the hides to form said organometallic complex, retanning the impregnated hides with a mineral-tanning agent selected from the group consisting of chrome-, aluminum-, and iron-tanning agents, and drying the retanned hides.

7. The method of making tanned animal hides water-repellent, which comprises impregnating said hides with a complex organometallic compound formed by interaction in situ of (1) an anionic water-miscible compound selected from the group consisting of (*a*) esters and amides of tricarboxylic and higher polycarboxylic organic acids and tribasic and higher polybasic inorganic acids, said esters and amides containing at least one organic hydrophobic waterproofing radical in the ester and amide moiety, and (*b*) condensation products of a high molecular weight unsaturated fatty acid with maleic acid, said compound containing at least two free, salt-forming groups capable of forming an organo-metallic complex with metallic ions in the mineral-tanning agent, and (2) a mineral-tanning agent selected from the group consisting of chrome-, aluminum- and iron-tanning agents, drying the impregnated hides and heating the dried hides to about 90° C.

8. The method of making mineral-tanned animal hides water-repellent, said hides being tanned with a mineral-tanning agent selected from the group consisting of chrome-, aluminum-, and iron-tanning agents, which comprises impregnating said hides with an anionic water-miscible compound selected from the group consisting of (*a*) esters and amides of at least tricarboxylic organic acids and at least tribasic inorganic acids, said esters and amides containing at least one organic hydrophobic water-proofing radical in the ester and amide moiety, and (*b*) condensation products of a high molecular weight unsaturated fatty acid with maleic acid, said compound containing at least two free, salt-forming groups capable of forming an organometallic complex compound with said mineral-tanning agent, the amount of said water-miscible compound being in excess of that required to combine with all of said mineral-tanning agent in the hides to form said organometallic complex, retanning the impregnated hides with a mineral-tanning agent selected from the group consisting of chrome-, aluminum-, and iron-tanning agents, drying the retanned hides and heating the dried retanned hides to about 90° C.

9. The method of making non-mineral-tanned leather water-repellent, which comprises impregnating said leather with an anionic water-miscible compound selected from the group consisting of (*a*) esters and amides of at least tricarboxylic organic acids and at least tribasic inorganic acids, said esters and amides containing at least one organic hydrophobic waterproofing radical in the ester and amide moiety, and (*b*) condensation products of a high molecular weight unsaturated fatty acid with maleic acid, said compound containing at least two free, salt-forming groups capable of forming an organometallic complex compound with a mineral-tanning agent, retanning the impregnated hides with a mineral-tanning agent selected from the group consisting of chrome-, aluminum-, and iron-tanning agents, and drying the retanned hides.

10. The method of making tanned animal hides water-repellent, which comprises impregnating said hides with a complex organometallic compound formed by interaction in situ of an anionic water-miscible salt of a tribasic acid ester, said acid ester containing at least one alkyl chain having 8 to 18 carbon atoms and at least two free, salt-forming groups capable of forming an organometallic complex with metallic ions in the mineral-tanning agent, and a chrome mineral-tanning agent, and drying the impregnated hides.

11. The method of making tanned animal hides water-repellent, which comprises impregnating said hide with a complex organometallic compound formed by interaction in situ of an anionic water-miscible salt of a tribasic acid ester, said acid ester containing at least one alkyl chain having 8 to 18 carbon atoms and at least two free, salt-forming groups capable of forming an organometallic complex with metallic ions in the mineral-tanning agent, and an aluminum mineral-tanning agent, and drying the impregnated hides.

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