

[54] **METHOD OF PREPARING
DRY-CLEANABLE SOIL-RESISTANT
LEATHERS**

[75] Inventor: **Vincent Joseph Cassella, Jr.**,
Audubon, Pa.

[73] Assignee: **Pennwalt Corporation**, Philadelphia,
Pa.

[22] Filed: **Mar. 22, 1972**

[21] Appl. No.: **237,217**

Related U.S. Application Data

[62] Division of Ser. No. 37,019, May 13, 1970, Pat. No.
3,668,124.

[52] **U.S. Cl.**..... **117/62.2, 117/142, 117/167**
[51] **Int. Cl.**..... **C14c 9/02, B44d 1/32**
[58] **Field of Search**..... **117/142, 90, 62.2,**
117/167; 8/94.22; 252/8.57

[56] **References Cited**

UNITED STATES PATENTS

2,693,996 11/1954 Von Fuchs..... 8/94.22
2,374,678 5/1945 Gruenwald..... 117/142 UX

2,934,450 4/1960 Brown..... 117/154 X
3,484,271 12/1969 Kaliski et al..... 117/62.1
3,351,643 11/1967 Hauptschein et al..... 117/142 X
2,892,673 6/1959 Heyden et al..... 8/94.22 X
2,974,000 3/1961 Retzsch et al..... 8/94.23

OTHER PUBLICATIONS

Hopkins et al., "Influence of Alkenyl Succinic Acid,"
JALCA 62, pp. 162-173 (1967).

Primary Examiner—William D. Martin
Assistant Examiner—Harry J. Gwinnell
Attorney—Stanley Litz

[57] **ABSTRACT**

A fatliquor composition useful for leather treatment
comprises a mixture of alkenyl substituted succinic
acid or succinic acid anhydride, sulfated fatty oil, and
an amine or amide. The leather is treated with an
aqueous emulsion of the fatliquor composition and
then with an aqueous solution of the chromium coordi-
nation complex of perfluoroalkyl-containing carbox-
ylic acid to provide a soil and water-repellent leather
that is resistant to loss of lubricity when drycleaned.

6 Claims, No Drawings

METHOD OF PREPARING DRY-CLEANABLE SOIL-RESISTANT LEATHERS

This is a division of application Ser. No. 37,019 filed May 13, 1970, now U.S. Pat. No. 3,668,124.

This invention relates to a composition and method for lubricating and imparting softness and soil and water repellency to leather. More particularly, this invention concerns treating leather with a fatliquoring composition comprised of a mixture of alkenyl succinic acid or acid anhydride, a sulfated fatty oil, and an organic, nitrogen-containing compound, such as an amine or amide, followed by treatment with a chromium coordination complex of a perfluoroalkyl-containing carboxylic acid.

There are several significant and important advantages achieved by the use of the composition and the practice of the method of the present invention. Leather treated according to this invention, especially suede garment leathers made of sheepskin or cow-hide split, can be drycleaned in conventional drycleaning equipment without loss of softness caused by extraction of the lubricating oils from the leather by the cleaning solvent. In addition to its resistance to extractability of lubricating (fatliquor) oils, leather treated according to this invention is notably resistant to water and oil-borne stains. Moreover, when staining does occur, the stain can be easily removed by a damp cloth or with aerosol spot removers. Leather garments made from leathers treated in accordance with the invention are especially attractive to consumers since problems long associated with such clothing are alleviated, for example, water spotting after wetting and the difficulty of removing stains, soils and dirt from the leather.

Moreover, an important advantage of this invention accruing to the tanner or manufacturer is that much less fatliquor composition is required to lubricate the leather compared to that required with the conventional fatliquors used prior hereto. For example, 0.5 to 1.5 percent by weight of the fatliquor lubricating composition of this invention, based on the weight of leather, will lubricate sheep skin garment suede to give a satisfactory soft hand and drape compared to 8 to 12 percent of conventional oils required in the present practice in the industry. Similarly, the amount of the fatliquor composition of this invention required to satisfactorily lubricate split garment leather is 4 to 6 percent of the leather weight compared to 18 to 26 percent required for conventional oils.

The fatliquor lubricating composition used in the first step of the leather treatment process of this invention comprises a mixture of from about 30 to about 90 parts by weight of alkenyl substituted succinic acid or alkenyl substituted succinic acid anhydride wherein the alkenyl group attached to the alpha carbon atom of the acid or anhydride has from about 12 to 24 (preferably 15 to 20) carbon atoms; from about 5 to about 60 parts (preferably 10 to 40) parts by weight of sulfated fatty oil, and about 5 to 25 (preferably about 10 to 15) parts by weight of an organic, nitrogen-containing compound selected from the group consisting of alkyl amines, alkanol amines, heterocyclic amines, aromatic amines, and alkyl amides. The alkenyl succinic acid or anhydride may of course be a mixture of acids or anhydrides having alkenyl groups of varying chain lengths within the aforesaid range.

The standard term "sulfated fatty oil" refers to those conventional fatliquoring oils containing at least 4 per-

cent by weight of combined sulfate (SO_3). Examples of such known, highly sulfated fatliquoring oils are the sulfated vegetable, fish, and animal fat oils such as sulfated olive oil, mahogany oil, cotton seed oil, corn oil, peanut oil, soy bean oil, palm oil, cod oil, neatsfoot oil, sperm oil and others known in the art. It has been found that the pure unsulfated fatty oils, as well as mineral oil, when substituted for the sulfated oil of the claimed composition, do not provide the desired results.

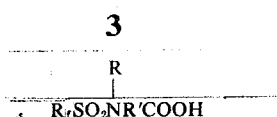
The organic, nitrogen-containing compound in the fatliquoring composition of this invention is necessary to aid in emulsification of the fatliquoring composition in the aqueous media which is normally used in leather treatment. Representative of such nitrogen containing compounds are alkyl amines, alkanol amines, aromatic amines, heterocyclic amines and alkyl amides, e.g., the mono-, bi-, and tri-alkyl amines, the methyl amines, hexyl amines octyl amines, decyl amines, i.e., wherein the alkyl group has up to about 12 carbon atoms; the hydroxyl-containing alkyl amines such as the mono-, bi- and tri-ethanol amines and propanol amines, methyl diethanol amine, 2-aminopropanol, dimethylamino ethanol, diglycol amine, and the like; heterocyclic amines such as morpholine and piperidine and the like; aromatic amines, such as aniline, toluidine, *n*-methylaniline and the like; and representative amides such as dimethylformamide, dimethylacetamide, diethylacetamide, dimethylpropionamide and the like.

The fatliquor composition of this invention as above described is a slightly viscous to very viscous oil in physical appearance. Preparatory to treatment of leather with this fatliquor composition, it is advantageously mixed with from about 300 to 700 parts by weight of water per hundred parts by weight of fatliquor composition, preferably at a temperature within the range of about 115° F. to about 130° F., with vigorous stirring, to provide an oil-in-water emulsion medium which is subsequently applied to the leather by conventional drumming techniques well-known to those skilled in the art of leather treatment. For example, the leather is treated with the fatliquor composition by contact therewith for from about 30 to 60 minutes at somewhat elevated temperatures, preferably ranging from about 115° F. to about 130° F. It is generally advantageous to first drum the washed skins in hot water to ensure they are thoroughly wetted prior to fatliquoring.

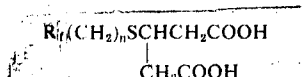
The second step of the process of this invention involves contacting the leather, which has previously been treated with the aforesaid lubricant composition, with a chromium coordination complex of a perfluoroalkyl carboxylic acid, wherein the perfluoroalkyl group (linear or branched chain) embodied therein desirably contains from about 6 to about 18 carbon atoms, preferably 9 to 15 carbon atoms. Representative complexes are described in U.S. Pat. No. 3,351,643 which discloses chromium coordination complexes of perfluoroalkyl acids of the structure



where R_f is perfluoroalkyl, R is hydrogen or alkyl having 1 to 4 carbon atoms and R' is alkylene having 1 to 6 carbon atoms; and U.S. Pat. No. 2,934,450 which describes chromium coordination complexes of perfluoroalkyl acids having the structure



where R_f is the perfluoroalkyl group, R is hydrogen or alkyl having 1 to 6 carbon atoms and R' is an alkylene group having from 1 to 12 carbon atoms. Other perfluoroalkyl carboxylic acids of this type which may be converted into chromium coordination complexes essentially in the manner described in the foregoing patents and used in the second step of the process of this invention are represented by the following (where n and m are integers as described in the references):



and the other fluoroalkyl acids described in U.S. Pat. No. 3,471,518; R_fCOOH as described in U.S. Pat. No. 3,311,566; $R_f(CH_2)_nCOOH$ as described in U.S. Pat. No. 2,951,051; $R_f(CH_2)_mS(CH_2)_nCOOH$ as described in U.S. Pat. No. 3,172,910; $R_fO(CF_2)_mCOOH$ and $R_fO(CF_2)_m(CH_2)_nCOOH$ as described in U.S. Pat. No. 3,453,333; $R_fO(CF(CF_3)CF_2O)_nCF(CF_3)COOH$ as described in U.S. Pat. No. 3,274,239 and U.S. Pat. No. 3,250,808; $R_f(CH_2)_nO(CH_2)_2COOH$ and other acids described in U.S. Pat. No. 3,231,604 and U.S. Pat. No. 3,145,222; and $R_fCH(OH)COOH$ described in U.S. Pat. No. 3,202,706, and other like fluoroalkyl acids.

The chromium coordination complexes of perfluoroalkyl carboxylic acids are conveniently water-soluble, and, therefore, dilute aqueous solutions thereof are advantageously used to treat the leather subsequent to the fatliquor treatment step described previously. For example, aqueous solutions containing from about 0.5 to 7 percent by weight of the chromium coordination complex are preferably used to give a pick-up of the chrome complex on the leather of approximately the same concentration based on the blue weight of the leather. The pH of the chromium complex treating solution will range from about 3 to 5.5, preferably from 3 to 3.5, and this pH is adjusted, if necessary, by the addition thereto of a small amount of an organic acid or mineral acid such as formic acid, acetic acid or sulfuric acid. The leather is treated with chromium coordination complex solution at a temperature in the range of about 100° to 130° F. for from about 15 to 60 minutes.

After drying, and, if desired, staking and buffing, the treated skins show unusually good repellency to water and oil spotting and resistance to oil and water-borne stains, in addition to being comparatively quite resistant to oil extraction in dry cleaning. The skins also show a pronounced improvement in softness, in hand and in drape, making them highly desirable for suede garment manufacture.

The following examples are presented to illustrate the invention and to demonstrate that all elements described therein are necessary in order to give the stated results. Unless otherwise stated, all amounts of ingredients referred to in the examples are given in parts by weight:

EXAMPLE 1

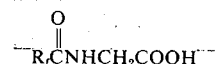
A fatliquor composition in accordance with this invention is prepared by blending 10 parts of morpholine with 80 parts of mixed alkenyl succinic acid anhydride wherein the alkenyl substituent ranges from C_{15}

4

to C_{20} ("Chevron ASA," a product of Chevron Chemical Company), and this is mixed with 10 parts of sulfated sperm oil containing approximately 7.0% combined sulfate ("Hydrol 80," product of Reilly-Whiteman-Walton Company.)

Tanned sheepskins taken from production following extract retanning are washed, short floated at 120° F., and drummed for 20 minutes. The emulsified fatliquor composition is added to the leather treatment wheel (1 percent based on the wet weight of the skins). The skins are drummed for 40 minutes at 120° F., and the float appears clear. The skins are then rinsed for 5 minutes at 110° F., horsed overnight (14-16 hours), and then set out (put through a wringer to remove excess water), tunnel dried overnight, milled and buffed.

The fatliquor treated skins are wet back for 30 minutes at 130° F. and again medium to short floated at 120° F. The float is adjusted to pH 3 to 3.5 with formic acid. Then 2.5 percent (based on weight of the blue skins) of a chromium coordination complex of a branched perfluoroalkyl acid (having the formula



where R_f (i.e., $(CF_3)_2CF(CF_2)_n$) is a mixture of from 9 to 15 fluoroalkyl carbon atoms, U.S. Pat. No. 3,351,643) is added to an equal amount of hot water (120° F.) and the mixture added to the drum. The skins are drummed 45 minutes after which time the bath is clear. The skins are rinsed at 100° F. for 5 minutes and then horsed. After a minimum of 2-3 hours, the skins are toggle dried and put through the final stages of staking and blocking.

The treated leather has excellent water and oil repellency properties. The leather is passed through a typical coin-operated dry-cleaning cycle and the results show there is a 9.1 percent loss of fatliquor lubricant in the dry-cleaning operation.

EXAMPLE 2

The procedure of Example 1 is repeated, except that the fatliquor composition added to the leather is 1 percent of the alkenyl substituted succinic acid anhydride ("Chevron ASA") without the addition of sulfated fatty oil and amine. The lubrication step is followed by treatment with 2 percent of the chromium coordination complex of the perfluoroalkyl-containing carboxylic acid as in Example 1. The loss in dry-cleaning of the fatliquor lubricant is significantly greater (23.8 percent) for this leather.

EXAMPLE 3

The procedure of Example 2 is repeated, except that the amount of alkenyl substituted succinic acid anhydride added to the leather is increased to 3 percent. This reduces the fat loss in dry cleaning to 8 percent. However, the treating materials do not penetrate the leather sufficiently and there is an unacceptable greasy deposit on the surface of the skin.

EXAMPLE 4

The fatliquoring treatment of Example 1 is repeated, using 8% by weight of fatty oils ("Nutreen ED, medium sulfated sperm oil containing 5.0 percent combined sulfate, and Nutreen X" neatsfoot oil base alkaline fatliquor containing 0.55 percent combined sulfate, prod-

ucts of Salem Oil and Grease Company). The treatment of the leather with the chromium coordination complex of the perfluoroalkyl-containing carboxylic acid is omitted. The fat loss after one dry-cleaning cycle is 65 percent of the lubricant originally applied.

EXAMPLE 5

50 parts of "Chevron ASA" are blended with 10 parts of morpholine and 40 parts of a sulfated mixture of fatty oils and alcohol fatty esters containing 4.0 to 4.4 percent combined sulfate (Reilly-Whiteman-Walton" 938X fatliquor"). The fatliquor composition is emulsified with water (120° F.), added to the wheel, and used to treat 100 pounds of split garment leather which had first been washed, short floated at 120° F. and drummed for 20 minutes. Ten percent of the fatliquor lubricant composition based on wet weight is taken up by the leather. The skins are drummed for 45 minutes, rinsed for 5 minutes at 110° F. and refloated (short) at 120° F. The float is adjusted to pH 3 to 3.5 with formic acid, and 2.5 percent of the chromium coordination complex used in Example 1 (based on blue weight of the skins) is added to an equal amount of hot water (120° F.), and the solution added to the wheel. The skins are drummed 45 minutes, after which the float is clear. The skins are water-rinsed for 5 minutes at 110° F., dumped, horsed overnight, hung dried at 100° F. for 5 hours, and then put through the final stages of staking and buffing. The skins show very good water and oil repellency as well as resistance to water and oil-borne stains. The skins are subjected to a coin operated drycleaning cycle operation and only 6.6 percent of the fatliquor lubricant is lost in the drycleaning.

I claim:

1. A method of preparing a stain resistant, water and oil repellent, dry-cleanable leather which comprises the

steps of contacting leather with an aqueous emulsion of a fatliquor lubricating composition comprising a mixture of from about 30 to about 90 parts by weight of alkenyl substituted succinic acid or alkenyl substituted succinic acid anhydride wherein the alkenyl group attached to the alpha carbon atom of the acid or anhydride contains from about 12 to 24 carbon atoms, from about 5 to about 60 parts by weight of sulfated fatty oil, and about 5 to 25 parts by weight of an organic nitrogen-containing compound selected from the group consisting of alkyl amines, alkanol amines, heterocyclic amines, aromatic amines, and alkyl amides, and then contacting the leather with an aqueous solution of a chromium coordination complex of a perfluoroalkyl-containing carboxylic acid wherein the perfluoroalkyl group has from about 6 to about 18 carbon atoms, said aqueous solution having a pH in the range of about 3 to 5.5; and drying the leather.

2. The method in accordance with claim 1 wherein the alkenyl group of the substituted succinic acid or anhydride has from 15 to 20 carbon atoms.

3. The method in accordance with claim 1 wherein the organic, nitrogen-containing compound is morpholine.

4. The method in accordance with claim 1 wherein there are from 10 to 40 parts by weight of sulfated fatty oil and about 10 to 15 parts by weight of the nitrogen-containing compound.

5. The method according to claim 1 wherein the perfluoroalkyl group of the carboxylic acid has from 9 to 15 carbon atoms.

6. The method according to claim 1 wherein the pH of the aqueous solution of perfluoroalkyl carboxylic acid is from 3 to 3.5.

* * * * *

40

45

50

55

60

65