United States Patent Office 2,950,950
Patented Aug. 30, 1960

2,950,950

OIL BASE FAT-LIQUOR COMPOSITION WITH POLYBASIC ACID ESTER AND METHOD OF USE

Jürgen Plapper, Rudi Heyden, and Günther Arnold, Dusseldorf, Germany, assignors to Bohme Fettchemie G.m.b.H., Dusseldorf, Germany, a corporation of Germany

No Drawing. Filed June 24, 1954, Ser. No. 439,144

Claims priority, application Germany June 27, 1953

10 Claims. (Cl. 8—94.23)

The present invention relates to a new and improved fat-liquor composition and more particularly to a fat-liquor composition for fat-liquoring chrome-tanned hides and to a process of fat-liquoring such hides.

Complex formation of chrome-tanning agents during the chrome-tanning process is ordinarily effected by the use of salts of aliphatic and aromatic mono- or polybasic carboxylic acids which may be substituted by sulfo groups, amino groups, phenolic hydroxyl groups and the like as well as by inorganic salts of sulfurous acid and phosphoric acid.

Thereby masked tanning takes place as it is characterized by greater plumpness of the leather, tight grain, and fine grain structure. Said characteristics are dependent upon the specific properties of the respective masking agent used. Chrome-tanning with concomitant use of oxalates, sulfites, or phosphates, yields, for instance, firm, compact, and firm grained leather. Formates produce soft loose grained leather, and phthalates yield leather of especially high plumpness and high chromic oxide content.

Such masking agents are also frequently applied during the neutralization step. Thereby acid residues of the chrome complex of strongly acid reaction, for instance, sulfate residues, are exchanged against acid residues of the masking agent, of weakly acid reaction, i.e., the acid residues of the masking agent enter into the chrome complex by displacing the normally present sulfate residues therein. As a result thereof the chrome complex is stabilized and does not give off acid residues of strongly acid reaction during and after a treatment with vegetable or synthetic tanning agents.

Such a procedure inhibits any troublesome subsequent souring of chrome leather tanned in combination with such vegetable or synthetic tanning agents.

The use of said masking agents during or after tanning reduces the strongly cationic charge of the leather surface. The thus treated leather can be more uniformly dyed by means of acid and substantive dyestuffs without overloading the leather surface, and especially its flank sections of porous or loose structure.

Formation of the dreaded coarse grain and cracking of said grain in connection with such combined tanning processes are avoided by treating the leather with masking agents during or after the chrome-tanning step proper. A fine grained leather is obtained thereby because the high absorptive power of purely chrome-tanned leather with respect to anionic, synthetic and vegetable tanning agents is markedly reduced by said treatment with masking agents.

It is one object of the present invention to provide a process of applying said masking agents to chrome-tanned leather and to improve the properties of such leather during the fat-liquoring step.

Another object of the present invention is to provide a fat-liquor composition which not only affects fat-liquoring but also influences the chrome complex by masking agents.

Other objects of the present invention and advantageous features thereof will become apparent as the description proceeds.

It was found that instead of adding masking agents to the chrome-tanning bath or the neutralizing bath, the chrome complex is also advantageously affected and the leather properties are considerably improved by adding suitable masking agents to the fat-liquor used in fat-liquoring chrome-tanned leather. Such masking agents are, for instance, sulfurous acid, phosphoric acid, formic acid, oxalic acid, adipic acid, di-adipic acid, tartaric acid, citric acid, 1,2,3,4-butane tetracarboxylic acid, phthalic acid, trimesic acid, mellitic acid, nitrilo triacetic acid, ethylene dinitrilo tetracetic acid, and others or their water soluble salts, polycarboxylic acids obtained by reacting maleic acid anhydride and unsaturated carboxylic acids and their sulfonation products.

Such masking agents are either added to the fat-liquor emulsion or a liquor oil is used which contains such masking compounds. Liquor oils which are especially suitable for this purpose are oils which contain oil-soluble acid esters or amides of said acids with higher molecular alcohols or amines, such as, for instance, monododecyl orthophosphoric acid ester, monooctadecyl citric acid ester, the monododecyl ester of nitrilo triacetic acid as well as the mono- or didodecyl ester of ethylene dinitrilo tetracetic acid, and other oil-soluble derivatives of said acids or their salts.

The above mentioned compounds exhibit not only an excellent masking effect but they also have good emulsifying and greasing properties. They are preferably added to liquor oils in amounts of about 2% to about 20% in place of other emulsifying agents or together with such other emulsifying agents. In this manner it is possible to change the mode of action of liquor oils which, as such, tend to yield softer chrome leather of loose grain in such a manner that leather with good compactness, firmness, plumpness, and tight and fine grain is obtained and their tendency to form softer leather is overcome.

Chrome-tanned leather which has been neutralized and fat-liquored by means of a liquor oil according to the present invention can readily be subjected to subsequent tanning with vegetable and synthetic tanning agents without any danger that the pH value would decrease too strongly. Due to the reduction of the positive charge of the surface of such chrome-tanned leather which was treated with a liquor oil according to the present invention, uniform absorption of anionic, synthetic, and vegetable tanning agents is achieved. The resulting leather has a fine grain.

When dyeing such chrome-tanned leather which has been fat-liquored with a liquor oil containing masking agents according to the present invention, the customary acid leather dyestuffs are much more uniformly absorbed. The surface and those sections of the hides which are of loose and porous structure (the flank parts) are not too strongly colored, because the dyestuffs penetrates the leather to a greater extent than when such leather is tanned in accordance with known methods.

According to the prescribed process the greasing of the leathers and the masking is performed simultaneously in the same operation. The tanning is performed in the usual manner well known, the drawbacks that occur in masking during the chrome tanning are obviated. The leathers show a smoother feel and a firmer grain. The masking agents according to the invention possess a double effect as they impart to the leather smoothness, plumpness, and a firm grain. Furthermore the oil soluble masking agents have a good dispersing power.

The following examples serve to illustrate the present invention, without, however, limiting the same thereto.

Example 1

A liquor is prepared from 40 parts of a sperm oil sulfonated with 20% sulfuric acid, 40 parts of unsulfonated sperm oil, 10 parts of mineral oil of a viscosity of 30–45 cp. St at 20° C., and 10 parts of the sodium salt of monododecyl orthophosphoric acid ester. Depending upon the thickness and the type of the leather to be fat-liquored, 1.2% to 3.5% (calculated for the shaving weight) of said liquor oil are used for fat-liquoring of chrome-tanned upper leather whereby the ratio of leather to liquoring bath is 1:2.0–2.5. Thereby a compact fine grained leather which is plump, especially in the flank sections, is obtained.

Example 2

A liquor oil is used as described in Example 1 which has additionally added thereto 15% of the cyclohexylamine salt of monooleyl orthophosphoric acid ester as emulsifying agent. In the preparation of tanned cowhide for clothing purposes, the leather is subjected, after chrome-tanning and neutralization, to a preliminary fat-liquoring treatment with about ⅓ of the total required amount of liquor oil of the above given composition (4–6%) and is then tanned with 3–6% of a vegetable tanning agent, dyed, subjected to an after-treatment with the residual ⅔ of said above mentioned liquor oil and is then processed in the customary manner to leather adapted for clothing purposes. This treatment yields plump and uniformly colored leather of good feel.

Example 3

A liquor oil is used as described in Example 1 and 2 to which 10% of the ammonium salt of a monocitric acid ester has been added. The fatty alcohol fraction used for esterifying said citric acid consists of coconut fatty alcohols of a chain length with 12–18 carbon atoms. Box calf leather, after chrome-tanning, normal neutralization and fat-liquoring with 1.1–1.3% of the above described liquor oil is then dyed in the customary manner with acid dyestuffs. Thereby the leather is uniformly and deeply colored even at the loose-structured and porous flank parts thereof. One may also first subject the leather to a preliminary treatment with ⅓ to ½ of the total required amount of the above described liquor oil whereafter the leather is dyed and then finally fat-liquored with the remaining liquor oil.

We claim:

1. The method of fat-liquoring chrome-tanned hides and skins, which comprises contacting said hides and skins with a non-aqueous fat-liquor composition comprising an oil base containing as a masking agent about 2 to 20% of an acidic higher aliphatic ester of a polybasic acid selected from the group consisting of tri- and tetrabasic acids, said ester containing at least two free acid groups and being soluble in said oil base.

2. The method of fat-liquoring chrome-tanned skins and hides, which comprises contacting said skins and hides with a non-aqueous fat-liquor composition comprising a sperm oil base containing as a masking agent, about 2 to 20% of an acidic higher aliphatic alcohol mono-ester of a polybasic acid, selected from the group consisting of tri- and tetrabasic acids wherein the alcohol radical contains from 12 to 18 carbon atoms in the carbon chain, said monoester containing at least two free acid groups and being soluble in said sperm oil base.

3. The method of fat-liquoring chrome-tanned skins and hides, which comprises contacting said skins and hides with a non-aqueous fat-liquor composition comprising a sperm oil base containing as a masking agent, about 2 to 20% of an acidic salt of an alcohol mono-ester of a polybasic acid selected from the group consisting of tri- and tetra-basic acids, wherein the alcohol radical contains from 12 to 18 carbon atoms in the carbon chain, said salt containing at least two free acid groups and being soluble in said sperm oil base.

4. The method of fat-liquoring chrome-tanned skins and hides, which comprises contacting said skins and hides with a non-aqueous fat-liquor composition comprising a sperm oil base containing as a masking agent about 2 to 20% of the sodium salt of the mono-dodecyl ester of orthophosphoric acid, said sodium salt being soluble in said sperm oil base.

5. The method of fat-liquoring chrome-tanned skins and hides, which comprises contacting said skins and hides with a non-aqueous fat-liquor composition comprising a sperm oil base containing as a masking agent about 2 to 20% of the cyclohexylamine salt of the mono-oleyl ester of orthophosphoric acid, said salt being soluble in said sperm oil base.

6. The method of fat-liquoring chrome-tanned skins and hides, which comprises contacting said skins and hides with a non-aqueous fat-liquor composition comprising a sperm oil base containing as a masking agent about 2 to 20% of the ammonium salt of coconut fatty alcohol mono-esters of citric acid, wherein the fatty alcohol radicals contain from 12 to 18 carbon atoms, said salt being soluble in said sperm oil base.

7. A fat-liquoring composition for chrome-tanned hides and skins, comprising an oil base and about 2 to 20% of a masking agent selected from the group consisting of acidic higher aliphatic alcohol mono-esters of polybasic acids, selected from the group consisting of tri- and tetra-basic acids wherein the alcohol radical contains from 12 to 18 carbon atoms, and salts thereof, said masking agent containing at least two free acid groups and being soluble in said oil base.

8. A fat-liquoring composition for chrome-tanned hides and skins, comprising a sperm oil base and, as a masking agent, about 2 to 20% of the cyclohexylamine salt of the mono-oleyl ester of orthophosphoric acid.

9. A fat-liquoring composition for chrome-tanned hides and skins, comprising a sperm oil base, and, as a masking agent, about 2 to 20% of the sodium salt of the mono-dodecyl ester of orthophosphoric acid.

10. A fat-liquoring composition for chrome-tanned hides and skins, comprising a sperm oil base and, as a masking agent, about 2 to 20% of the ammonium salt of a fatty alcohol ester mixture of citric acid wherein the fatty alcohol radicals contain from 12 to 18 carbon atoms in the carbon chain, wherein the esters of said mixture contain at least two free acid groups.

References Cited in the file of this patent

UNITED STATES PATENTS

1,407,449	Tommerson	Feb. 21, 1922
2,115,509	Jaeger	Apr. 26, 1938

FOREIGN PATENTS

139,140	Australia	Oct. 23, 1950

OTHER REFERENCES

J.A.L.C.A., April 1949, p. 229.

Calgon Data, Calgon Inc., 1949, pp. 15 and 16.

Progress in Leather Science, 1920–45, London, 1948, p. 562.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,950,950 August 30, 1960

Jürgen Plapper et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 5, for "cp." read -- c --.

Signed and sealed this 19th day of September 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents

USCOMM-DC