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[54] **PROCESS FOR TANNING WITH A MULTIVALENT METAL AND AN ORGANIC COMPOUND**

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[58] **Field of Search** 8/94.26, 94.29, 94.22, 8/94.23

[56] **References Cited**

UNITED STATES PATENTS

2,178,874	11/1939	Hervey	8/94.26
2,693,996	11/1954	Von Fuchs	8/94.22
2,950,950	8/1960	Plapper et al	8/94.23
3,010,780	11/1961	Plapper et al	8/94.26
3,811,832	5/1974	Briggs	8/94.26

FOREIGN PATENTS OR APPLICATIONS

788,539	1/1958	Great Britain	8/94.22
836,808	6/1960	Great Britain	8/94.26

OTHER PUBLICATIONS

Revue Technique des Industries du Cuir, Sept. 15, 1955, page 205.

Revue Technique des Industries du Cuir, February 1953, page 30.

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[57] **ABSTRACT**

A process for tanning hides or skins comprises firstly treating the hide or skin with a basic salt of a multivalent metal, secondly treating the hide or skin under alkaline conditions with an organic compound having a long chain aliphatic group and at least one reactive group capable of entering into a complex with a basic salt of a multivalent metal, and thirdly treating the hide or skin with a salt of a multivalent metal.

31 Claims, No Drawings

PROCESS FOR TANNING WITH A MULTIVALENT METAL AND AN ORGANIC COMPOUND

This invention relates to the production of leather.

In U.S. application Ser. No. 132,580, filed Apr. 8, 1971, and now U.S. Pat. No. 3,811,832 there is described and claimed a process for the tanning of a hide or skin by treatment with a basic salt of a multivalent metal, and then with a reaction medium containing a water-soluble salt of a dibasic organic acid, said water-soluble salt being one that forms an alkaline solution in water, in an amount sufficient to maintain an alkaline pH in the reaction medium.

Leather which has been treated with a basic salt of a multivalent metal, that is "mineral tanned", has a pH in water in the range 3 to 5. The effect of adding a salt of a dibasic organic acid is to raise the pH to within the range 7.5 to 8.5. Such conditions are well outside the normal practice in the tanning industry. It has now been found that, provided the alkaline conditions are maintained, certain other organic compounds can also usefully be employed in the above-mentioned process. The resulting leathers on re-tanning are found to have improved hydrophobic properties.

According to the present invention a process for the tanning of a hide or skin comprises firstly treating the hide or skin with a basic salt of a multivalent metal, secondly treating the hide or skin under alkaline conditions with an organic compound having a long chain aliphatic group and at least one reactive group capable of entering into a complex with a basic salt of a multivalent metal, and thirdly treating the hide or skin with a salt of a multivalent metal.

Treatment with the organic compound is preferably carried out at a pH from 7.5 to 9. An aqueous solution of the organic compound is prepared and adjusted to the required pH by addition of suitable organic bases or inorganic alkalis. The alkali or base need not react with the organic compound, and weak alkalis such as sodium carbonate or ammonia have been found to be particularly suitable. It is usually found that the optimum value of pH is around 8.2 to 8.5. Preferably the leather is washed and neutralised throughout its whole thickness after tanning with the basic salt of a multivalent metal and prior to treatment with the organic compound, for example, with a weak alkali such as sodium bicarbonate, ammonium bicarbonate, ammonia or mixtures thereof. This neutralisation may be preceded by treatment with a salt of phthalic, formic or other weak acid.

The process of tanning with a basic salt of a multivalent metal can be carried out on stock with the hair or wool intact, or on hides and skins that been suitably prepared for tanning by conventional pre-tanning process, or that have previously been tanned, for example, by a vegetable tanning process (vegetable tanned crust stock). Suitable hides and skins that can be treated include, for example, bovine stock and sheep-skins.

Suitable basic salts of multivalent metals which can be used in the tanning process include particularly basic salts of metals having a valency of three or more, e.g. chromium, aluminium, zirconium and cerium. Salts of mineral acids are usually preferred, especially sulphuric acid. Particularly good results have been obtained using basic chromium sulphate, which can, for example, be prepared by adding sodium carbonate to a solution of chromium sulphate or chrome alum. The

basic salt of a multivalent metal may be "masked" with certain organic acid salts i.e. treated to form a mixed salt of modified reactivity but still capable of reacting with the organic compound.

The quantity of basic salt used is usually sufficient to give up to about 3.5% by weight (calculated as metal oxide) based on the dry weight of the hide or skin. Particularly good results have been obtained using a quantity of basic salt sufficient to give from 1.5 to 5.0% by weight of metal oxide based on the dry weight of the hide or skin.

The organic compound contains at least one and preferably two or more long chain aliphatic groups which preferably contain a chain of from six to thirty-six carbon atoms. Increasing the length of the aliphatic carbon chain or the number of aliphatic carbon chains in the compound is often found to give improved flexibility, perspiration resistance and water-shedding properties. The compound may contain one or more reactive groups which can, for example, be chloro, nitro, sulphonate, phosphate, carbonate, borate, citrate, thiocyanate, sulphate, amino or carboxyl groups.

Preferably the organic compound contains two or more reactive groups which for best results should be separated by a chain of at least six carbon atoms.

Mixtures of different organic compounds may be used provided that they do not react together and are stable under the reaction conditions.

Amongst many suitable organic compounds there may be mentioned alkali metal, ammonium or organic base salts of long chain aliphatic carboxylic acids for example, oleic, palmitic and stearic acids; half esters of long chain dicarboxylic acids; salts of sulphonated or sulphate long chain mono carboxylic acids, for example the ammonium, sodium and potassium salts of sulphonated or sulphated oleic and palmitic acids; sulphonated or sulphated triglycerides, for example medium sulphated cod oil, and lightly sulphated cold test neatsfoot oil; and long chain aliphatic amino acids.

The quantity of organic compound used is usually not less than 3% based on the shaved weight of the leather and is preferably from 3 to 8%. In many instances, it has been found useful in promoting penetration to carry out the reaction of the leather with the organic compound in the presence of a water-soluble or water miscible alcohol or a liquid hydrocarbon. Suitable alcohols include benzyl alcohol and cyclohexanol, and suitable hydrocarbons include white spirit. After reaction with the organic compound, the leather is either further treated with a salt of a multivalent metal or dried to produce a crust stock.

The crust stock is easily wettable, and may similarly be converted to the waterproof state by treatment with a salt of a multivalent metal. This can be a basic salt, for example, the basic salt of chromium, aluminium, zirconium or cerium initially used for tanning or any other suitable basic salt, or a normal salt, for example, a copper, zinc, zirconium, aluminium or nickel salt, particularly a sulphate. This after-treatment confers the hydrophobic properties to the final product. The quantity of basic or normal salt used is usually such as to give from 1.0 to 3.0% by weight (calculated as metal oxide) based on the shaved weight of the leather. Prior to treatment with the salt of a multivalent metal the leather may be rinsed and lightly acidified on the outer surface to pH 4.6 to 5.0. the metal salt used may be

"masked" with a formate, acetate phthalate, citrate or other suitable salt.

The organic compounds used in the present invention do not usually form basic salts with multivalent metals which are soluble in water, and thus the tanning of the hide or skin with the basic salt of the multivalent metal and the treatment with the organic compound is preferably carried out by immersing the hide or skin in an aqueous solution of the basic salt of the multivalent metal, bringing the pH of the hide or skin in the reaction liquor up to the desired value and then adding the organic compound.

The process is preferably carried out in a tanning drum, since a low water/load ratio is desirable to accelerate the reactions. Suitable drum speeds have been found to be from 6 to 12 r.p.m., and an optimum speed can easily be found by experiment. The process may be completed in acceptable tannery time schedules and for each stage of the process the time for completion of the reaction is usually from 2 to 24 hours.

The reactions usually proceed at an acceptable rate at room temperature but if necessary elevated temperatures, for example up to about 50°C, can be used.

Dyeing may be carried out prior to the further treatment with a salt of a multivalent metal or subsequently. With some dyestuffs it is advisable to use a cold float.

After treatment by the process of the invention, the leather may be neutralised if necessary and subjected to any of the normal finishing operations provided that the formulations used do not contain excessive amounts of surfactants or hydrophilic materials. The conventional fat-liquoring step can often be substantially reduced in amount and sometimes omitted altogether. Softer leathers are made by treating with a small amount of hydrocarbon solvent, e.g. white spirit, or a small amount of a straight oil e.g. neatsfoot or sperm oil emulsified in the organic reactants prior to application.

The invention is illustrated by the following Examples:

EXAMPLE 1

This Example describes a tanning process according to the invention leading to the production of a leather having improved water-proofing properties.

A tanned chrome leather is prepared by treating pickled stock with from 1.5 to 3.5% by weight of chromic oxide in the form of a one-third basified chromium sulphate to a shrinkage temperature of about 100°C. The leather is aged for twenty-four hours and freed from uncombined material by washing. After levelling the substance by splitting and/or shaving, the leather is placed in a water float in a tanning drum and the equilibrium pH raised to 7.5 to 9 with sodium bicarbonate or ammonia.

In the same solution and at the same pH various organic compounds are added as detailed in Table I below until such time as complete penetration is obtained. This can be judged by a colour reaction on the cut edge with 5% w/w copper sulphate. When the liquor is exhausted and the penetration of the reactant found complete, the leather is washed thoroughly with water and the wash water drained off.

It is advisable at this stage to reduce the pH of the leather without disturbance of the unco-ordinated reactive groups in the leather. For this purpose a small amount of a weak acid or phthalic anhydride may be added using about 30 – 50% water as drum float for about five minutes. In this manner the surface pH of the leather is reduced to about 4.6. At the same time or immediately afterwards 5% of a neutral salt such as sodium sulphate is added to restrain the rate of subsequent re-tannage.

The leather is then treated with a further 6 to 8% by weight of basic chromium sulphate powder (containing 24 to 26 % by weight of Cr_2O_3) to produce a hydrophobic leather. After complete penetration as tested by an indicator such as bromocresol green, the resultant leather is washed free of electrolytes and dried out.

The results are given in Table I. Water-proofing is judged by SLP22 (IUP/10) which is the accepted test of the International Union of Leather Chemists Societies. This is expressed as the time taken for water to penetrate the sample and the amount of water taken up expressed as a percentage of the sample weight. In the result a running period of 240 minutes is taken as evidence of water-proofing and figures quoted at less than 240 minutes indicate that the leather had wet through.

The amounts of organic compounds are given as percentages of the shaved or split weight of the wet chrome leather containing approximately 60% water.

TABLE I

Compound	% age	pH	Dynamic water uptake (DWU) time (minutes)	% H_2O absorbed
1. Ammonium oleate	3	8.2	150	30
	5	8.2	270	26
	5	8.2	240	34
2. Ammonium salt of sulphated oleic acid	4	8.5	90	23
	6	8.5	270	26
(as above but degreased)	4	8.5	180	25
	6	8.5	240	26
3. Ammonium salt of sulphated oleic acid (different source)	6	7.5	120	120
	6	8.5	210	35
	8	7.5	240	128
	8	8.5	240	24
4. Potassium salt of sulphated oleic acid	6	7.5	140	97
	6	8.5	150	20
	8	7.5	150	108
	8	8.5	240	21

TABLE I – Continued

Compound	% age	pH	Dynamic water uptake (DWU) time (minutes)	% H_2O absorbed
5. Sulphated oleic acid sodium finish 80% approx.	6	8.2 – 8.4	240	13
	8	8.2 – 8.4	240	19
as above but with 5% benzyl alcohol	6	8.2 – 8.4	240	12
	8	8.2 – 8.4	240	12
6. Medium sulphated cod oil 80%	2	8.2 – 8.4	70	18
	4	8.2 – 8.4	165	18
	6	8.2 – 8.4	240	22
7. Lightly sulphated cold test neatsfoot oil 85%	4	8.2 – 8.4	120	20

Example 5 is on chrome side (bovine stock). All other experiments are on chromed sheep skins. Controls processed by normal chrome tanning techniques give dynamic water penetration periods in the order of ten minutes. This Example shows that tanning according to the process of the invention leads to the production of a highly waterproof leather. In addition it is found that samples treated at pH 8.5 also have excellent perspiration resistance.

EXAMPLE 2

This Example describes further processes according to the invention for the production of a leather having improved water-proofing properties.

The procedure of Example 1 is repeated except the leather is neutralised to a pH of 8.2 to 8.4 prior to the application of the organic compound. Re-tannage is carried out using a mixture of 5% sodium sulphate and 6% basic 33% chromium sulphate powder (25% Cr_2O_3) based on the shaved weight of the leather or 6% basic aluminium chloride (66% basic) 25% Al_2O_3. In each case, half of the samples were degreased with petroleum ether. The results are given in Table II. Percentages of organic compounds used are based on the shaved weight of the leather containing 60 – 65% water.

TABLE II

Compound		Re-tannage: Chrome DWU time (minutes)	Chrome DWU % H_2O absorbed	Chrome DWU Degreased time (minutes)	Chrome DWU Degreased % H_2O absorbed	Aluminium DWU time (minutes)	Aluminium DWU % H_2O absorbed	Aluminium DWU Degreased time (minutes)	Aluminium DWU Degreased % H_2O absorbed
Ammonium oleate	4%	300+	19	240+	16	270+	45	90	100
	5%	240+	17	240+	20	240+	100	90	46
	6%	240+	19	240+	19	180+	51	270+	58
Sulphated cod oil	6%	210	24	180+	14	120	126	270	39
Sulphated neatsfoot oil	6%	60	11	180	22	60	24	270+	41

These results show that both chromium and aluminium re-tannages lead to waterproof leathers, and the hydrophobic properties of the chrome leather are unaffected by degreasing.

I claim:

1. A process for the tanning of a hide or skin which comprises firstly treating the hide or skin with a basic tanning salt of a multivalent metal, secondly treating the hide or skin with an organic compound having a long chain aliphatic group while maintaining alkaline pH conditions during such treatment said compound having at least one reactive group capable of entering into a metal complex with the basic tanning salt of a multivalent metal, and thirdly treating the hide or skin with a salt of a multivalent metal at an acid pH.

2. A process according to claim **1**, in which the treatment with the organic compound is carried out at a pH of from 7.5 to 9.

3. A process according to claim **2**, in which the required pH is maintained by addition of a weak alkali.

4. A process according to claim **1**, in which the leather is washed and neutralised throughout its whole thickness after tanning with the basic tanning salt of a multivalent metal and prior to treatment with the organic compound.

5. A process according to claim **1**, in which the basic tanning salt of a multivalent metal is a basic salt of chromium, aluminum, zirconium or cerium.

6. A process according to claim **1**, in which the basic tanning salt is a mineral acid salt.

7. A process according to claim **1**, in which the quantity of the basic tanning salt of a multivalent metal used is sufficient to give from 1.5 to 5.0% by weight of metal oxide based on the dry weight of the hide or skin.

8. A process according to claim **1**, in which the long chain aliphatic group contains a chain of from six to 36 carbon atoms.

9. A process according to claim **8**, in which the organic compound is one that contains two or more long chain aliphatic groups.

10. A process according to claim **1**, in which the reactive group of the organic compound is a chloro, nitro, sulphonate, phosphate, carbonate, borate, citrate, thiocyanate, sulphate, amino or carboxyl group.

11. A process according to claim **1**, in which the organic compound contains two or more reactive groups separated by a chain of at least six carbon atoms.

12. A process according to claim **1**, in which the organic compound is an alkali metal, ammonium or or-

ganic base salt of a long chain aliphatic carboxylic acid, a half ester of a long chain aliphatic dicarboxylic acid, a salt of a sulphonated or sulphated long chain mono carboxylic acid, a sulphonated or sulphated triglyceride, or a long chain aliphatic amino acid.

13. A process according to claim **1,** in which the quantity of organic compound used is from 3 to 8% based on the shaved weight of the leather.

14. A process according to claim **1,** in which the treatment with the organic compound is carried out in the presence of a water-soluble or water miscible alcohol or a liquid hydrocarbon.

15. A process according to claim **1,** in which the hide or skin is immersed in an aqueous solution of the basic tanning salt of the multivalent metal, the pH of the hide or skin in the aqueous solution is brought up to the desired value, and the organic compound is then added.

16. A process according to claim **1,** in which after treatment with the organic compound, the hide or skin is further treated with a basic salt of a multivalent metal.

17. A process according to claim **16,** in which the basic salt of a multivalent metal that is used to further treat the hide or skin is a basic salt of chromium, aluminum, zirconium or cerium.

18. A process according to claim **16,** in which the quantity of basic salt used for the further treatment is from 1.0 to 3.0% by weight, calculated as metal oxide, based on the shaved weight of the leather.

19. A process according to claim **1,** in which, after treatment with the organic compound, the hide or skin is further treated with a normal salt of a multivalent metal.

20. A process according to claim **19,** in which the normal salt is a salt of copper, zinc, zirconium, aluminium or nickel.

21. A process according to claim **19,** in which the quantity of normal salt used for the further treatment is from 1.0 to 3.0% by weight, calculated as metal oxide, based on the shaved weight of the leather.

22. A leather tanned with a basic tanning salt of a multivalent metal and containing on adsorbed complex of an organic compound, having a long chain aliphatic group and a single reactive group, and a salt of a multivalent metal, said leather being produced by the process of claim **1.**

23. A leather according to claim **22,** in which the basic tanning salt of a multivalent metal is a basic salt of chromium, aluminium, zirconium or cerium.

24. A leather according to claim **22,** in which the organic compound is an alkali metal, ammonium or organic base salt of a long chain aliphatic carboxylic acid, a half ester of a long chain dicarboxylic acid, or a long chain aliphatic amino acid.

25. A leather according to claim **22,** in which the salt of a multivalent metal that is used to further treat the leather is a basic salt of chromium, aluminium, zirconium or cerium.

26. A leather according to claim **22,** in which the salt of a multivalent metal that is used to further treat the leather is a normal salt of copper, zinc, zirconium, aluminium or nickel.

27. A leather tanned with a basic tanning salt of a multivalent metal and containing chemically bonded residues of a complex of an organic compound, having a long chain aliphatic group and two or more reactive groups, and a salt of a multivalent metal, said leather being produced by the process of claim **1.**

28. A leather according to claim **27,** in which the basic tanning salt of a multivalent metal is a basic salt of chromium, aluminium, zirconium or cerium.

29. A leather according to claim **27,** in which the organic compound is a salt of a sulphonated or sulphated long chain mono carboxylic acid, or a sulphonated or sulphated trigylceride.

30. A leather according to claim **27,** in which the salt of a multivalent metal that is used to further treat the leather is a basic salt of chromium, aluminium, zirconium or cerium.

31. A leather according to claim **27,** in which the salt of a multivalent metal that is used to further treat the leather is a normal salt of copper, zinc, zirconium, aluminium or nickel.

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