Patented June 28, 1938 2,122,133

UNITED STATES PATENT OFFICE

2,122,133

IRON-TANNED LEATHER

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No Drawing. Application July 16, 1936, Serial No. 90,918. In Germany July 24, 1935

16 Claims. (Cl. 149—5)

The present invention relates to iron-tanned leather, a process for producing same and preparations suitable for carrying out this process.

Contrasted with tanning with chromium and aluminium salts, it is not possible when tanning with inorganic iron salts to prepare tanning solutions ready for use by increasing the basicity because iron hydroxide is thereby precipitated. It has already been proposed gradually to neutralize the acid content of the iron salt solutions during the tanning; leather is thus obtained which has the advantage of not swelling during the washing out, but which on the other hand dries hard and blank and has very bad stability when stored. Better leather is obtained by tanning with complex iron compounds which contain in the complex organic acids having one or more carbon atoms, the resulting iron-tanned leather being after-treated with synthetic tanning agents if desired. It has also been proposed to add albumen degradation products to the tanning liquor. All these processes have disadvantages, however, and are therefore not used in practice.

We have now found that leather of good color, compact grain and good touch is obtained in a simple manner by tanning unhaired hides with complex iron compounds which contain organic substitution products of ammonia in the complex. A complex iron compound of the said kind which may be mentioned by way of example is hexaurea iron chloride of the formula

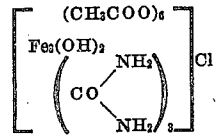
$$[Fe(H_2N—CO—NH_2)_6]Cl_3$$

It may be formed by adding the calculated amount of urea to a solution of iron chloride. A 15 per cent solution of the said salt has a pH value of 2.5 and may be directly used for tanning after the addition of sodium chloride, sulphate or acetate.

Instead of urea, other organic nitrogen compounds may be combined in the complex of the iron salts, as for example acid amides, such as formamide and acetamide, condensation products of aldehydes with amines or ammonia, such as hexamethylene tetramine, and also urethanes, amines and similar compounds.

A part of the nitrogenous compounds combined in the complex of the said tanning agents may also be replaced by other compounds, as for example weak organic acids, whereby the liquor acquires a darker color. The absorption of the tanning agent from the liquor may therefore be observed especially well by the lightening in color which occurs.

Valuable tanning agents to be employed according to the present invention are also the salts of the hexaacetato-dihydroxy-carbamido-triferric base, for example



The salts of this base can be obtained in good yields from ferric salts, soluble acetates and urea in aqueous solutions, even when using a small excess of urea, by adding alkaline substances before, during or after the reaction. It is preferable to employ an excess of urea which is by about 35 to 50 per cent above the theoretical amount. There may thus be introduced into the complex from 1 to 3 molecules of urea, depending on the amount of urea employed. The preparation of the said salts may be effected in aqueous solutions of such concentrations that the reaction product is immediately precipitated. Yields of up to 97 per cent of the theory are thus obtained. Among alkaline substances which are added to the reaction solution we may mention caustic soda solution, caustic potash solution, soda, ammonia, amines and the like. The reaction is preferably carried out at temperatures of below 35° C. At higher temperatures there easily occurs formation of water-insoluble basic acetates, whereby the yields are diminished.

The thorough tanning of unhaired hides with the complex iron salts in question takes place in a few hours and the leather may be rinsed immediately, but preferably after storage for a short time, neutralized if necessary and finished off in the usual manner. In order to protect sensitive leather, neutralization may also be effected during the tanning by the addition of sodium carbonate, sodium bicarbonate, sodium acetate or sodium phosphate solution without iron hydroxide being precipitated.

Iron-tanned leathers having good properties may also be obtained by not starting from the ready-made iron complex salts referred to above, but causing the same to be formed only in the tanning solution by adding the starting materials necessary for the preparation of the iron complex salts to the solution separately in any desired sequence.

The tanning with the solution so prepared is effected in the same manner as in the case of ready complex iron-compounds. A leather is ob-

tained which is stable to swelling, of a pale color, and stable when stored and has a good touch and a high yield.

The leather obtained according to the present invention may be after-treated with synthetic tanning agents, preferably those which are neutral or slightly acid, whereby in many cases a softer and fuller leather is obtained; if it is desired to obtain a tan-colored leather, synthetic tanning agents containing hydroxy groups must be avoided.

Instead of treating the unhaired hides with synthetic tanning agents after the thorough tanning with the said iron salts, the two treatments may be carried out simultaneously. In this manner the inorganic acid radicle situated outside the complex of the iron salt is wholly or partly replaced by the radicles of acids which have a high affinity for the hide. Finally complex iron salts of organic acids may also be prepared from the complex iron salts with inorganic acid radicles capable of dissociation and the alkali salts of synthetic tanning agents, as for example from hexa-urea iron chloride or its components and the sodium salt of a condensation product derived from napththalene sulphonic acid and formaldehyde; the complex iron salts thus obtainable may be isolated and by tanning yield directly the leather which otherwise would first be obtained by aftertanning with synthetic tanning agents.

As further acids having a high affinity for the hide there may be employed for example the condensation products of aromatic sulphonic acids, such as phenol sulphonic acids, cresol sulphonic acids, with aldehydes and ketones of low molecular weight, and also the reaction products of urea and formaldehyde on the said condensation products. Sulphonic acids such as are obtained by the treatment of the residues obtainable in the purification of anthracene with concentrated sulphuric acid may also be mentioned as agents for forming salts for the complex compounds according to this invention.

With the said sulphonic acids of high molecular weight, there are formed readily water-soluble complex iron compounds which are obtained either as solid glassy masses or thick viscous pastes and which after redissolution in water directly yield solutions having excellent tanning properties. After drumming for from about 5 to 10 hours, the thorough tanning is completed and a leather is obtained which has a full touch, which is well colored and which has a compact grain; it may be fatted and finished off in the usual manner. The leather also exhibits a yield (up to about 50 per cent) which is very high for an iron-tanned leather; even suspenders may be prepared with the said tanning substances by the methods usual in vegetable tanning.

The following examples will further illustrate how the said invention may be carried out in practice, but the invention is not restricted to these examples. The parts are by weight.

Example 1

100 parts of unhaired calf hides which have been pickled in the usual manner are drummed for a few minutes with 100 per cent of water and 2 per cent of common salt and then 10 per cent of hexaurea iron chloride (Barbieri, C. 1913, II. 1034), 5 per cent of common salt and 100 per cent of water are added. Drumming is continued until thorough tanning has taken place. At intervals of 2½ hours for a period of about 8 hours, soda solution is added until the whole is neutral to congo. The leather is then rinsed while cold and hot, fatted and finished off in known manner.

Example 2

100 parts of unhaired cattle hides which have been pickled in the usual manner are drummed for a few minutes with 100 per cent of water and 2 per cent of common salt. There are then added 25 per cent of the complex iron salt obtained by concentrating in vacuo an aqueous solution of iron chloride and acetamide in the molecular proportions of 1:6, 12.5 per cent of common salt and 100 per cent of water. The whole is further drummed in the vat for 8 hours after which complete and thorough tanning has been effected. The leather is aftertreated for 2 hours with 100 per cent of water and 10 per cent of the neutral sodium salt of a condensation product derived from naphthalene sulphonic acid and formaldehyde and finished off in the usual manner. A pale colored leather having a good touch is thus obtained which is stable in storage.

Example 3

3 equivalents of the acid condensation product derived from napththalene sulphonic acid and formaldehyde are added to a solution containing 1 molecular proportion of a complex salt prepared in the usual way from iron chloride and hexamethylene tetramine. The solution is rendered slightly acid to congo by the addition of caustic soda solution. By concentration in vacuo, the tanning agent is obtained as a thick, viscous, red syrup.

Tanning is carried out by drumming 100 parts of unhaired cattle hides, which have been pickled in the usual manner, with 100 per cent of water and 2 per cent of common salt for a few minutes, then adding 12 per cent of the iron tanning agent, dissolved in 36 per cent of water, and 6 per cent of common salt and drumming the whole in a vat until complete and thorough tanning has taken place, which is the case after from 6 to 10 hours depending on the nature of the unhaired hides. The leather is then rinsed while cold and hot and fatted and finished off in the usual manner. A compact, smooth-grained, full leather is thus obtained.

Example 4

By adding 6 molecular proportions of formamide to an aqueous solution of 1 molecular proportion of iron chloride, hexaformamide iron chloride is obtained. There are stirred into the solution 3 equivalents of the acid condensation product derived from naphthalene sulphonic acid and formaldehyde, the solution being rendered slightly acid to congo by the addition of caustic soda solution. By concentration in vacuo a thick, viscous, red syrup is obtained which may be used as a tanning agent in the manner described in Example 3.

Example 5

30 equivalents of the sodium salt of the condensation product derived from naphthalene sulphonic acid and formaldehyde are added to an aqueous solution of 12.5 molecular proportions of iron chloride, 20 molecular proportions of sodium acetate and 15 molecular proportions of urea; the resulting solution is concentrated in vacuo at from 30° to 40° C. whereby a thick, viscous syrup is obtained which yields a solid glassy mass when

dried in the air. The latter has an appearance similar to natural tanning agents. It may be used as described in Example 3.

Example 6

3 molecular proportions of the sulphonation product of residues from the purification of anthracene are added to an aqueous solution of 1 molecular proportion of hexaurea iron chloride, the whole being rendered slightly acid to congo by the addition of caustic soda solution. By concentration in vacuo, the tanning agent is obtained in the form of a thick, viscous syrup which may be used as described in Example 3.

Example 7

100 parts of unhaired cattle or calf hides which have been pickled in the usual manner are drummed for a few minutes with 100 parts of water and 2 parts of common salt and then 40 parts of water, 3.5 parts of iron chloride, 5.6 parts of sodium acetate, 2.5 parts of urea, 0.7 part of soda and 6 parts of the acid sodium salt of the condensation product from naphthalene-sulphonic acid and formaldehyde are added in any sequence, and drumming is continued in a vat until thorough tanning has taken place. The leather is then rinsed while cold and hot, fatted and finished up in the usual manner.

Example 8

100 parts of unhaired cattle hide pickled in the usual manner are fulled for some minutes with 100 parts of water and 2 parts of common salt and then drummed for from about 5 to 8 hours with 40 parts of water, 6 parts of common salt, 4.6 parts of iron chloride and 5 parts of acetamide until thorough tanning has been attained. Then 6 parts of the neutral salt of the condensation product of naphthalene sulphonic acid and formaldehyde are added. Drumming is continued for another 2 hours and the leather then finished up in the usual manner.

Example 9

100 parts of unhaired calf hide which has been pickled in the usual manner are drummed for a few minutes with 100 parts of water and 2 parts of common salt, then drummed for from about 5 to 8 hours in a vat with 40 parts of water, 6 parts of common salt, 4.6 parts of iron chloride and 3 parts of acetamide until thorough tanning has been attained. A solution of 6 parts of the neutral salt of the condensation product from naphthalene sulphonic acid and formaldehyde and 2 parts of sodium alanine is then gradually added in small portions and drumming is continued for another 2 hours. The leather is fatted and finished up in the usual manner.

Example 10

A mixture of 54.4 parts of crystalline sodium acetate, 19 parts of urea, 5.3 parts of sodium hydroxide and 15 parts of water is slowly stirred, while cooling with water, into a solution of 32.4 parts of iron chloride in 26 parts of water. There is avoided heating above 35° C. The hexa-acetato-dihydroxy-tricarbamido - triferric chloride immediately precipitates as a red crystalline precipitate which after filtering off by suction is dried in vacuo or in current of air at 35° C. There is obtained a yield of 97 per cent of the theory (calculated with reference to the amount of iron employed). The complex salt may be obtained in a completely pure form by a single recrystallization from alcohol. It is suitable for tanning, for instance as described in Example 3 or 7.

What we claim is:

1. The process for the preparation of iron-tanned leather which comprises treating unhaired hides with a solution of a complex iron compound which contains an organic substitution product of ammonia in the complex.

2. The process for the preparation of iron-tanned leather which comprises treating unhaired hides with a solution of a complex iron compound which contains an organic substitution product of ammonia in the complex and subjecting the leather obtained to an aftertreatment with synthetic tanning agents.

3. The process for the preparation of iron-tanned leather which comprises treating unhaired hides with a solution of a complex iron compound which contains an organic substitution product of ammonia in the complex and the outer valencies of which are at least partially saturated with an acid having affinity for hides.

4. The process for the preparation of iron-tanned leather which comprises treating unhaired hides with a solution of a complex iron compound which contains in the complex an organic substitution product of ammonia and a weak acid.

5. The process for the preparation of iron-tanned leather which comprises treating unhaired hides with a solution of a complex iron compound which contains in the complex an organic substitution product of ammonia and a lower aliphatic acid.

6. The process for the preparation of iron-tanned leather which comprises treating unhaired hides with a solution of a complex iron compound which contains urea in the complex.

7. The process for the preparation of iron-tanned leather which comprises treating unhaired hides with a solution of a salt of the hexaacetato - dihydroxy - tricarbamido - triferric base.

8. The process for the preparation of iron-tanned leather which comprises treating unhaired hides with a solution in which a complex iron compound containing an organic substitution product of ammonia in the complex is formed from its components during the treatment.

9. Tanning agents comprising a complex iron compound which contains in the complex an aliphatic substitution product of ammonia.

10. Iron-tanning agents comprising a complex iron compound which contains urea in the complex.

11. Iron-tanning agents comprising a salt of the hexaacetato-dihydroxy-tricarbamido-triferric base.

12. Iron-tanning agents comprising a complex iron compound which contains in the complex an organic substitution product of ammonia and the outer valencies of which are at least partially saturated with an acid having affinity for hides.

13. The process for the preparation of iron-tanned leather which comprises treating unhaired hides with a solution of a salt of a hexaacetato-dihydroxy-carbamido-triferric base.

14. Iron-tanning agents comprising a salt of the hexaacetato-dihydroxy-carbamido-triferric base.

15. Iron-tanning agents comprising a complex

iron compound which contains in the complex an organic substitution product of ammonia containing at least one amido group and the outer valencies of which are at least partially saturated with an acid having affinity for hides.

16. Iron-tanning agents comprising a complex iron compound which contains in the complex urea and the outer valencies of which are at least partially saturated with an acid having affinity for hides.

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