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3,415,935

HIDE CURING COMPOSITION CONTAINING AN ORGANIC TIN COMPOUND, REDUCING AGENT AND HEXAMETHYLENE-TETRAMINE

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No Drawing. Filed Dec. 14, 1964, Ser. No. 418,284
Claims priority, application Germany, Dec. 14, 1963,
D 43,177

10 Claims. (Cl. 424—288)

ABSTRACT OF THE DISCLOSURE

Applicant cures hides, skins and pelts with a sodium chloride mixture containing up to 10% of an organo-tin compound, up to 1% of a reducing agent such as SO₂, sodium nitrite, sodium bisulphites, benzene sulfonic acid or ascorbic acid, and up to 30% of hexamethylenetetramine. The reducing agent stabilizes the tin compounds, of which the following were expressly enumerated: tri-n-butyltin-acetate, -benzoate, and -salicylate, dibutyltin-succinate, triethyltin-laurate, bis-(tributyltin)-oxide, bis-(triethyltin)-sulphide, octyltin-trihexaoate, tribenzylphenyltin, triethyltin-phenoxy and triisopropyltin-pentachlorophenolate. Polyglycol type emulsifiers and alkali can be added to the mixture. Pieces of calfskin, 100 x 100 mm., were treated with these mixtures and rolled up, tied up with rubber rings or kept in screw-top jaws. Skins, spotted and stained by mineral stains due to poor preservation were also tested. The latter skins were sometimes decolorized while all skins were adequately preserved. A mixture of .01% tri-n-butyltin-acetate, .5% NaNO₂, 5% hexamethylenetetramine and 7.4% SO₂ was particularly good as a preservative.

This invention relates to curing, more particularly to curing agents for skins and pelts and to a method of curing skins and pelts.

The present invention provides curing agents by which both the discolourations, such as red and violet discolourations, produced by bacteria, especially halophilic bacteria (phycomycetes, actinomycetes and other types of schizomycetes), and the formation of mineral salt stains or spots can be prevented.

Hitherto, skins have been treated with various mixtures of sodium chloride and bacteriostatic agents, with a more or less strongly disinfectant action, without a satisfactory result.

From the known state of the art it was not to be expected that a satisfactory result would be obtained by the additional use of disinfectants during the salting of hides or skins with sodium chloride, since it had been found that, for example, disinfectants based on phenols or quaternary ammonia bases lost considerably in activity.

Mineral salt stains are caused by deposits of water-insoluble phosphorus-containing calcium and/or magnesium compounds in the fibrous texture of the skin. Owing to the discolourations and stains produced by bacteria and minerals during the curing, the skins suffer a reduction in quality, so that they are either completely unusable or are unusable for certain purposes, such as for the production of buckskin leather and glove leather.

The purpose of the present invention is to find a means which prevents the stains and incrustations of skins, pelts and the like caused both by bacteria and by minerals.

It has been found surprisingly that organo-tin compounds mixed with sodium chloride do not lose their bac-

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tericidal or bacteriostatic action during the salting of hides, while the prevention of the formation of mineral salt stains probably depends on a colloidochemical action of the organo-tin compounds applied together with sodium chloride. It was also surprisingly found that the activity and the stability of the tetravalent organo-tin compounds may be increased by the presence of a reducing agent. The action of the tetravalent organo-tin compounds is retained even during a fairly long period of curing or storage. Examples of known reducing agents, which do not have a harmful effect on the process going on during the salting of the hides, are nitrites, for example sodium nitrite, bisulphites such as sodium bisulphite, benzene-sulphinic acid and ascorbic acid.

By the additional use of an organic complex-forming compound, such as hexamethylenetetramine, or a combination of a complex-forming compound and another reducing substance such as SO₂, a stabilisation and intensifying of the action of the curing agent are equally attained.

A further increased action is also obtained by the use of small amounts of a surface-active substance, for example of the polyglycol type.

The curing agent for hides, pelts and the like according to the invention therefore consists of sodium chloride and an organo-tin compound of the general formula:



in which R₁, R₂, R₃ and R₄ represent the same or different organic residues linked to the tin via carbon atoms, up to three of which may be replaced by organic or inorganic groups not linked via carbon atoms. Compounds of this type are, for example, tri-n-butyltin-acetate, -benzoate, -salicylate, dibutyltin-succinate, triethyltin-laurate, bis-(tributyltin)-oxide, bis-(triethyltin)-sulphide, octyltin-trihexaoate, tribenzylphenyltin, triethyltin-phenoxy or triisopropyltin-pentachlorophenolate. The curing agent also suitably contains a reducing agent and/or a complex-forming compound and/or a surface-active substance. In addition to sodium chloride, for example in the form of rock salt, sea salt, saltworks salt or common salt, other known mineral curing salts or curing salt mixtures, for example sodium chloride-sodium sulphate mixtures and so on, can be used together with the tetravalent organic tin compounds for the purposes of the invention.

According to one form of the invention, the curing agent contains, referred to sodium chloride, 0.003 to 10% by weight, preferably 0.01 to 1% by weight of the organo-tin compound, 0.009 to 30% by weight, preferably 0.03 to 3% by weight of hexamethylenetetramine and 0.03 to 1% by weight, preferably 0.2 to 0.5% by weight of the reducing agent.

Especially good results are obtained when the skins are salted with sodium chloride which contains 0.01% of a tri-n-butyltin compound, such as tri-n-butyltin-benzoate, bis-(tributyltin)-oxide, tri-n-butyltin-acetate and so on, 0.5% of sodium nitrite, 0.5% of hexamethylenetetramine with a sulphur dioxide content of 7.4% and 0.1% of emulsifying agent, for example of the polyglycol type.

The curing of the skins should be effected as far as possible in their fresh state in the time between the flaying and further treatment, for example tanning. Before the curing, the components of the mixture according to the invention are intimately mixed with salt and the mixture is applied, for example by sprinkling, on the skins. Since the activity of the separate components is not influenced by the method of application to the skins, the

object of the mixing is chiefly to make possible an easier manipulation.

A wet curing is also possible. In addition, the sodium chloride may be treated with known anti-caking agents as well as with the usual denaturants, for example soda, naphthalene and mineral oils. Especially favourable results are obtained when soda is used in amounts up to 5% by weight, preferably 2 to 4% by weight, since soda on the one hand has the most favourable reciprocal action with the components of the curing agent and on the other hand increases the action of the curing agent. The stabilised organo-tin compounds have no harmful effect on the processing of the skins after their curing. Apart from this, they have the advantage that they themselves do not lose their activity in the subsequent soaking process, and that they check the rotting during the soaking process which in some circumstances proceeds very rapidly.

Examples

A series of experiments was effected to test the curing agent according to the invention. For carrying out the experiments, unaltered and spotted salted calfskin, for example skin with red and violet discolouration, was cut into pieces of size 100 x 100 mm. The pieces of unspotted unaltered skin were then prepared in a different way, as is seen from the following Table I, and in each case brought together with a piece of spotted skin so that the flesh sides were superposed. These pairs of pieces were tightly rolled up for storage, tied up with rubber rings and kept in a screw-top jar. The pieces of skin were thus stored in an atmosphere like that prevailing in the cellars for the utilisation of skins, where the salted skins lie in piles.

The altered, spotted skin used appeared a uniform light red on the flesh side and was strewn with countless dark-red to violet stains in the form of dots, which were firmly fixed in the skin, while the light red colour appeared to adhere more to the sodium chloride crystals.

In Table I the experimental results are grouped together. The amounts of the components of the curing agent are indicated which serve for the control of the red and violet discolouration. For the salting, 500 g. of sodium chloride per kg. of fresh skin were used.

Table II gives experiments which were carried out with spotted skin; it is interesting to discover how far staining already present can be eliminated. It may be concluded from the table that red discolouration present can be permanently removed.

The two experiments reproduced in Table III were for the purpose of deciding whether the formation of salt stains can be avoided or cancelled with reducing substances. The lightening of the underlying part of the skins confirmed that they can. Moreover, the few brown points which were previously on the piece of skin could not be found after the experiments.

In a further series of experiments, the salting process was imitated. Fresh undressed calfskin was sprinkled with common salt on the flesh side, rolled up and tied. A small piece of stained skin was simultaneously rolled up with it. The amount of common salt used corresponded to half the weight of the skin and the salt contained the following additions in each case:

- (1) 0.01% of tri-n-butyltin-acetate
- (2) 0.001% of tri-n-butyltin-acetate
- (3) 0.5% of hexamethylenetetramine with a content of 7.4% of sulphur dioxide
- (4) 0.5% of sodium nitrite
- (5) 0.01% of tri-n-butyltin-acetate and 0.5% of sodium nitrite
- (6) 0.01% of tri-n-butyltin-acetate, 0.5% of sodium nitrite, 0.5% of hexamethylenetetramine with a content of 7.4% of sulphur dioxide.

An addition of 0.001% of tri-n-butyltin-acetate to the common salt is not sufficient to prevent a red and violet colouration. 0.1% of tri-n-butyltin-acetate, even without reducing agent and hexamethylenetetramine, prevents all discolouration and stain or spot formation. The skin sample which had been salted with sodium chloride which contained an addition of 0.01% of tri-n-butyltin-acetate, 0.5% of sodium nitrite and 0.5% of hexamethylenetetramine with a content of 7.4% of sulphur dioxide appeared particularly good. The skin sample which had been treated with pure sodium chloride was in by far the worst condition.

TABLE I.—EXPERIMENTS ON THE CURING OF CALFSKIN

	Treatment of the sound, salted skin with (amounts given for 1 kg. of skin)—	Appearance of the prepared skin after five weeks contact with stained skin
20	0.0750 g. tri-n-butyltin-benzoate. 0.1500 g. alkylphenylpolyglycol ether. 0.2375 g. hexamethylenetetramine. 0.0075 g. sulphur dioxide.	No attack, skin soft, pliable. Colour: quite light surface.
25	0.0375 g. tri-n-butyltin-benzoate. 0.0750 g. alkylphenylpolyglycol ether. 0.1896 g. formaldehyde. 0.1188 g. hexamethylenetetramine. 0.0038 g. sulphur dioxide.	No attack, skin soft, pliable. Colour: whole surface light.
30	0.0750 g. tri-n-butyltin-benzoate. 0.1500 g. alkylphenylpolyglycol ether. 0.2375 g. hexamethylenetetramine. 0.0075 g. sulphur dioxide.	No attack, skin soft, pliable. Colour: whole surface slightly grey.
35	0.0375 g. tri-n-butyltin-benzoate. 0.0750 g. alkylphenylpolyglycol ether. 0.1188 g. hexamethylenetetramine. 0.0038 g. sulphur dioxide.	No attack, skin soft, pliable. Colour: whole surface slightly grey.
	NaCl without addition.	Very strong red and violet colouration.
	0.0365 g. tri-n-butyltin-oxide. 17.5 g. soda.	Red discolouration, skin dry.
40	0.0725 g. tri-n-butyltin-oxide. 17.5 g. soda.	Weak red discolouration, skin dry.
	0.05 g. tri-n-butyltin-acetate. 17.5 g. soda.	Red discolouration, skin dry.
	0.1 g. tri-n-butyltin-acetate. 17.5 g. soda.	Very weak red discolouration, skin dry.
45	0.075 g. tri-n-butyltin-acetate. 1.0 g. hexamethylenetetramine. 1.25 g. sodium nitrite. 17.5 g. soda.	No attack, skin less dry, still pliable. Colour: fresh, very light.
	0.05 g. tri-n-butyltin-benzoate. 17.5 g. soda.	Red discolouration, skin dry.
50	0.1 g. tri-n-butyltin-benzoate. 17.5 g. soda.	No attack, skin dry.
	0.05 g. tri-n-butyltin-benzoate. 0.01 g. alkylphenylpolyglycol ether. 0.5 g. sodium nitrite. 17.5 g. soda.	Very weak red discolouration, skin soft, pliable.
55	0.05 g. tri-n-butyltin-benzoate. 0.1 g. alkylphenylpolyglycol ether. 2.5 g. sodium nitrite. 17.5 g. soda.	No attack, skin soft, pliable. Colour: fresh.
60	0.05 g. tri-n-butyltin-benzoate. 0.10 g. alkylphenylpolyglycol ether. 0.50 g. hexamethylenetetramine. 15.0 g. soda.	Isolated red spots, skin soft, pliable.
65	0.05 g. tri-n-butyltin-benzoate. 0.10 g. alkylphenylpolyglycol ether. 0.50 g. hexamethylenetetramine. 1.00 g. sodium nitrite. 15.00 g. soda.	No attack (after a further month's storage (6 months) weak red colouration at the edge). Skin: soft, pliable. Colour: fresh.
70	0.05 g. tri-n-butyltin-benzoate. 0.10 g. alkylphenylpolyglycol ether. 1.50 g. hexamethylenetetramine. 1.25 g. sodium nitrite. 17.5 g. soda.	No attack (not even after a further month's storage (6 months)). Skin: soft, pliable. Colour: fresh.
75	0.075 g. tri-n-butyltin-benzoate. 0.10 g. alkylphenylpolyglycol ether. 0.50 g. hexamethylenetetramine. 1.25 g. sodium nitrite. 17.5 g. soda.	No attack (not even after a further month's storage (6 months)). Skin: soft, pliable. Colour: fresh.

TABLE I.—EXPERIMENTS ON THE CURING OF CALF-SKIN—Continued

Treatment of the sound, salted skin with (amounts given for 1 kg. of skin)—	Appearance of the prepared skin after five weeks contact with stained skin
0.075 g. tri-n-butyltin-benzoate. 0.10 g. alkylphenylpolyglycol ether. 0.50 g. hexamethylenetetramine. 1.25 g. Sodium nitrite.	No attack (not even after a further month's storage (6 months)). Skin: soft, pliable. Colour: fresh.
0.05 g. tri-n-butyltin-benzoate. 0.10 g. alkylphenylpolyglycol ether. 1.50 g. hexamethylenetetramine. 1.25 g. ascorbic acid or sodium hydrogen sulphite or benzenesulphonic acid. 17.5 g. soda.	No attack (not even after a further month's storage (6 months)). Skin: soft, pliable. Colour: fresh.
0.075 g. tri-n-butyltin-salicylpoly-glycol ether. 0.50 g. hexamethylenetetramine. 1.25 g. sodium nitrite. 17.5 g. soda.	No attack (not even after a further month's storage (6 months)). Skin: soft, pliable. Colour: fresh.

When tri-n-butyltin-salicylpolyglycol ether is used, an emulsifying agent is not necessary.

TABLE II.—EXPERIMENTS ON THE CURING OF CALFSKIN

Treatment of stained, salted skin with (amounts given for 1 kg. of skin)—	State of the skin at the start of the experiment	Appearance of the treated skin after standing for five weeks
Rinsed with an aqueous solution of— 0.060 g. tri-n-butyltin-benzoate. 0.120 g. alkylphenylpolyglycol ether. 0.300 g. Formalin. 0.190 g. hexamethylenetetramine. 0.033 g. sulphur dioxide and afterwards lightly salted with pure common salt.	Red discolouration. Red discolouration, one corner violet discolouration.	Skin soft, pliable. Colour: whole surface very light to white. Skin soft, pliable. Colour: very light to white violet discolouration has remained.
Sprinkled with 100 g. of NaCl, which contains 1/10 of the amounts of the previous experiment of tri-n-butyltin-benzoate, alkylphenylpolyglycol ether, Formalin, hexamethylenetetramine and sulphur dioxide.	Slight red discolouration.	Skin soft, pliable. Colour: slight red discolouration (practically unchanged).
Sprinkled with 100 g. of NaCl, which contains 0.1% of tributyltin-acetate.	Slight red discolouration.	Skin soft, pliable. Colour: very light, almost white
Treated in places according to Experiment 3 (Table I).	Red discolouration.	Treated place slightly grey to light. Surrounding part red and weak, violet colouration.

TABLE III.—EXPERIMENTS ON THE CURING OF CALFSKIN

Treatment of stained, salted skin with (amounts given for 1 kg. of skin)	State of the skin at the start of the experiment	Appearance of the skin after standing for five weeks
Sprayed with 70 g. of isopropanol which contained 10% of water and 9% of sulphur dioxide (alcohol evaporated).	Strong red and violet discolouration.	No alteration, but lower part of skin lightened.

What we claim is:

1. A curing composition for skins, hides and pelts comprising 0.003 to 10%, a tin organic compound having the general formula



wherein R_I , R_{II} , R_{III} and R_{IV} are the same or different organic radicals bonded to the tin via carbon atoms, a maximum of three of said radicals being linked to the tin atom by an atom other than carbon, 0.003 to 1% by weight of a reducing agent and 0.003 to 30% by weight of hexamethylenetetramine, all weights being based on the weight of the sodium chloride.

2. Composition as defined in claim 1 in which the tetravalent tin atom is disposed in the cation of an organic salt of the group consisting of oxides, sulphides, phenolates and carboxylic acids.

3. The composition as defined in claim 1 wherein the tetravalent tin compound contains more than one tin atom linked to carbon atoms of a multi-valent organic radical.

4. The composition as defined in claim 1 wherein the tetravalent tin compound is selected from the group consisting of tri-n-butyl-tin-acetate, -benzoate, -salicylate, dibutyltin - succinate, triethyltin - laurate, bis-(tributyl-tin)-oxide, bis-(triethyl-tin)-sulphide, octyltin-trihexaoate, tribenzylphenyl-tin, triethyl - tin - phenoxide or triisopropyltin-pentachloro-phenolate.

5. The composition as defined in claim 1 wherein the tetravalent tin compound is a trialkyl tin salt of a carboxylic acid.

6. The composition as defined in claim 1 further containing a reducing agent.

7. Composition of claim 1 further containing a reducing agent selected from the group consisting of alkali metal nitrite, sulphur dioxide, alkali metal sulfite, formaldehyde, Formalin, benzene sulfinic acid and ascorbic acid.

8. The composition as defined in claim 1 in which hexamethylene tetramine is mixed with sulfur dioxide.

9. The composition as defined in claim 1 further containing a small quantity of sodium carbonate.

10. A curing composition for hides, skins and pelts comprising sodium chloride containing a small quantity in the range of 0.003 to 10% of a tin compound selected from the group consisting of: tri - n - butyl - tin - acetate, -benzoate, -salicylate, dibutyl - tin - succinate, triethyl-tin-laurate, bis - (tributyl - tin) - oxide, bis-(triethyl-tin)-sulphide, octyl - tin - trihexaoate, tribenzylphenyl-tin, triethyl-tin-phenoxide or triisopropyl - tin pentachloro - phenolate, 0.009 to 30% by weight of hexamethylene tetramine, 0.2 to 0.5% by weight of a reducing agent, up to about 7.4% of sulfur dioxide referred to the hexamethylene tetramine and a small quantity of an emulsifying agent.

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U.S. Cl. X.R.

8—94.15, 94.18