

Use of 2-mercapto-pyridine N-oxide

The present application relates to the use of 2-mercapto-pyridine N-oxide and/or a metal complex thereof for the preservation of animal skins and leather.

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2-Mercapto-pyridine N-oxide and its use as a preservative for cosmetics are known (Microbicides for the Protecting of Materials, Baulens; 1993 Chepron & Hall, pages 294-300).

- 10 It has now surprisingly been found that 2-mercapto-pyridine N-oxide, its salt and metal complexes permit excellent and permanent protection of the animal skins and leather from microbial attack during production and storage thereof.

- The application therefore relates to the use of 2-mercapto-pyridine N-oxide and/or
15 its salts and/or metal complexes for the preservation of animal skins and leather.

- 2-Mercapto-pyridine N-oxide is preferably used in combination with at least one further active ingredient suitable for the protection of animal skins and leather. In particular, mercaptobenzothiazole, methylene bithiocyanate, thiocyanatomethyl-
20 thiobenzothiazole (TCMTB), octylisothiazolinone, N-cyclohexylbenzothiophene-2-carboxamide s,s-dioxide and preferably phenolic compounds are suitable as further active ingredients for combination with 2-mercapto-pyridine N-oxide.

- These combinations have outstanding and synergistic properties and are likewise
25 the subject of the application.

- Suitable phenolic active ingredients are preferably phenol derivatives, such as tribromophenol, trichlorophenol, tetrachlorophenol, nitrophenol, 3-methyl-4-chlorophenol, 3,5-dimethyl-4-chlorophenol, phenoxyethanol, dichlorophene, o-
30 phenylphenol, m-phenylphenol, p-phenylphenol, 2-benzyl-4-chlorophenol, 2,4-dichloro-3,5-dimethylphenol, 4-chlorothymol, chlorophene, triclosan, fenticlor and ammonium, alkali metal and alkaline earth metal salts thereof and mixtures thereof.

- 35 Preferred 2-mercapto-pyridine N-oxide salts and metal complexes are the sodium and potassium salts and copper and zinc complexes.

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Combinations of 3,5-dimethyl-4-chlorophenol, 2-benzyl-4-chlorophenol, p-chloro-m-cresol (CMC) and/or o-phenylphenol (OPP) as phenolic components and 2-mercapto-pyridine N-oxide and/or its alkali metal and alkaline earth metal salts and its metal complexes are preferred.

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Particularly preferred combinations are the combinations of OPP and/or CMC with 2-mercapto-pyridine N-oxide and/or with its abovementioned salts and complexes.

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In particular, mixtures containing CMC and 2-mercapto-pyridine N-oxide Na salt and optionally OPP and their use according to the invention are preferred.

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The mixing ratios of 2-mercapto-pyridine N-oxide are in general 1 part by weight to 5 to 200, preferably 10 to 100, in particular 12 to 50, parts by weight of the further active ingredients or active ingredient mixtures.

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The ratio of the further active ingredients, in particular of the phenolic compounds, with one another may be widely varied and can be readily determined by customary experiments. In the case of a mixture of, for example, OPP and CMC, the ratio is preferably 1:1 to 1:5.

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The abovementioned active ingredient and the mixtures of the active ingredients are generally used in the form of formulations. The concentration for use is preferably 0.1 to 1% of active ingredient or active ingredient mixture, relative to the skins or leather to be protected.

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The compositions formed during formulation preferably contain 10 to 50% of the active ingredient or of the active ingredient mixture. In general, the compositions contain, as further components, 10 to 30% of alkali metal hydroxides and/or alkaline earth metal hydroxides; 1 to 20% of ionic and/or nonionic emulsifiers; 5 to 30% of organic solvents, such as, in particular, glycols, ketones, glycol ethers and alcohols, such as ethanol, methanol, 1,2-propanediol, n-propanol or 2-propanol, and 0-0.5% of aromas and fragrances. The remainder to 100% is water.

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According to the invention, the active ingredient and the active ingredient mixtures and the compositions which can be prepared therefrom are used according to generally customary methods of use in leather production, for protecting animal skins from attack and damage by microorganisms. Of particular interest is the fact

5 that members of the species *Aspergillus niger*, *Aspergillus repens*, *Hormoconis resinae*, *Penicillium glaucum* and *Trichoderma viride*, *Penicillium* species, such as *P. citrinum* or *P. glaucum*, *Paecilomyces variotii*, *Cladosporium* species, such as *Mucor* species, such as *Mucor mucedo*, *Rhizopus* species, such as *Rhizopus oryzae*, *Rhizopus rouxii*, are completely and permanently suppressed.

The following Examples serve for illustrating the invention and are not limited to this.

Example 1

- 5 Agar plates are contaminated with conidia of the species *Aspergillus niger*, *Aspergillus repens*, *Penicillium glaucum*, *Trichoderma viride* and *Hormoconis resinae*. Wet chrome leathers treated with mixture I, II and mixture III (wet blue) are then placed on top and incubated for 28 days at 95% relative humidity and 20 to 30°C.

Mixture I

30 parts by weight of p-chloro-m-cresol
13 parts by weight of o-phenylphenol

Mixture II

30 parts by weight of p-chloro-m-cresol
13 parts by weight of o-phenylphenol
1.2 parts by weight of 2-mercapto-
pyridine N-oxide Na salt

Mixture III

37 parts by weight of p-chloro-m-cresol
1.2 parts by weight of 2-mercapto-
pyridine N-oxide Na salt

- 10 The wet blues preserved with the mixture I exhibit growth of mould on the test specimens after an incubation time of only 10 days. In the case of mixture II and III, no attack is found after an incubation time of 28 days.

Example 2

Formulation I

- 27 parts by weight of p-chloro-m-cresol
5 12 parts by weight of o-phenylphenol
1.2 parts by weight of 2-mercapto-pyridine N-oxide Na salt
12 parts by weight of NaOH
14.2 parts by weight of 1,2-propanediol
Remainder to 100 parts by weight water

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Formulation II

- 37 parts by weight of p-chloro-m-cresol
1.2 parts by weight of 2-mercapto-pyridine N-oxide Na salt
10.5 parts by weight of NaOH
15 14 parts by weight of 1,2-propanediol
Remainder to 100 parts by weight water

Formulation III

- 30 parts by weight of p-chloro-m-cresol
20 1.2 parts by weight of 2-mercapto-pyridine N-oxide Na salt
8.5 parts by weight of NaOH
14 parts by weight of 1,2-propanediol
Remainder to 100 parts by weight water

Patent Claims

1. Use of 2-mercapto-pyridine N-oxide and/or its salts and/or its metal complexes for the preservation of animal skins and leather.
2. Process for the protection of animal skins and leather from microbial attack, characterized in that 2-mercapto-pyridine N-oxide is added to animal skins or leather or allowed to act on animal skins or leather.
3. Composition containing 2-mercapto-pyridine N-oxide and at least one further active ingredient suitable for the protection of animal skins and leather.
4. Composition according to Claim 3, containing, as additional active ingredient, at least one of the compounds mercaptobenzothiazole, methylene bithiocyanate, thiocyanatomethylthiobenzothiazole, octylisothiazolinone, N-cyclohexylbenzothiophene-2-carboxamide s,s-dioxide and/or a phenolic compound.
5. Composition according to Claim 4, containing, as a phenolic compound, tribromophenol, trichlorophenol, tetrachlorophenol, nitrophenol, 3-methyl-4-chlorophenol, 3,5-dimethyl-4-chlorophenol, phenoxyethanol, dichlorophene, o-phenylphenol, m-phenylphenol, p-phenylphenol, 2-benzyl-4-chlorophenol, 2,4-dichloro-3,5-dimethylphenol, 4-chlorothymol, chlorophene, triclosan, fenticlor and ammonium, alkali metal and alkaline earth metal salts thereof and mixtures thereof.
6. Composition according to Claim 5, containing o-phenylphenol and/or p-chloro-meta-cresol.
7. Composition according to at least one of Claims 3 to 6, containing, in addition to 2-mercapto-pyridine N-oxide, at least one further active ingredient suitable for the protection of animal skins and leather, alkali metal hydroxides and/or alkaline earth metal hydroxides, ionic and/or nonionic emulsifiers, solvents and optionally aromas and fragrances.



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8. Use of compositions according to Claims 3 to 7 in the and for the processing of animal skins.
 9. Animal skins, leather and products which are obtained or used in leather production, containing 2-mercapto-pyridine N-oxide.
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